

"THEORIE DES GRAPHS STOCHASTIQUES APPLIQUEE A LA
SYNTHESE ET A LA DEGRADATION ALEATOIRES DES
COMPOSES MACROMOLECULAIRES MULTIFUNCTIONNELS"

THEORY OF STOCHASTIC GRAPHS APPLIED TO THE RANDOM
SYNTHESIS AND DEGRADATION OF MULTIFUNCTIONAL
MACROMOLECULAR COMPOUNDS

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Ann. Chim., Vol. 1, 1966, p. 271-302

Translated by SCITRAN (Scientific Translation)
P. O. Box 5456, Santa Barbara, Calif.
93103

Prepared for and issued by the Jet Propulsion Laboratory
California Institute of Technology, Pasadena, Calif.
Under NASA contract NAS 7-100.

(NASA-TT-F-14504) THEORY OF STOCHASTIC
GRAPHS APPLIED TO THE RANDOM SYNTHESIS AND
DEGRADATION OF G. Champetier (Scientific
Translation Service) Jun. 1972 80 p CSCL

N72-33137

Unclas
07D G3/06 43706

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Translation of "Theorie des graphes stochastiques ap-
pliquee a la synthese et a la degradation ale-
atoires des composes macromoleculaires
multifunctionnels", Annales de
Chimie, Vol. 1, 1966,
pp. 271-302.



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 JUNE 1972

I

THEORY OF STOCHASTIC GRAPHS APPLIED TO THE
RANDOM SYNTHESIS AND DEGRADATION OF MULTIFUNCTIONAL
MACROMOLECULAR COMPOUNDS

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"Science is built of facts as a house is built of stones, but an accumulation of facts is no more science than a pile of rocks a house."

(H. Poincaré, Science and Hypothesis)

INTRODUCTION

If the remarkable properties of macromolecular substances are related to their large size, they depend no less closely on the structure of their macromolecular lattices. Thus, one is led to distinguish different classes of polymers according to the dimensionality of the lattices.

While the synthesis of one-dimensional or linear polymers through polymerization or polycondensation of bifunctional monomers leads to (usable) products soluble in appropriate solvents, three-dimensional polymers obtained from monomers — of which all or a part has a functionality of more than two — are infusible and insoluble in all solvents which do not degrade them.

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Thesis for doctorate in Physical Sciences, Paris, 1966.

The generally sudden appearance of these properties is evidenced by the massive coagulation of the reaction medium and seems to depend only on its composition: the phenomenon of gelification.

The interpretation and anticipation of this phenomenon have led to numerous studies and the propounding of theories, the most elaborate of which are not always subject to easy experimental verification, while the simplest ones necessarily involve disregarding certain very obvious data, such as the existence of intramolecular reactions in particular.

Thus, we have been led to propose a theoretical interpretation of the behavior of multifunctional macromolecular systems, chiefly from both a structural and stochastic point of view based on elementary data from the theory of graphs involving the axiomatic definition of the important concepts of intermolecular and intramolecular reactions. These notions, related to the number of molecules and the number of cycles, respectively, enable us through a topological study of the lattice to arrive at a definition of its three-dimensional nature, while the evolution of the lattice may be interpreted in terms of a statistical study of the connections which may occur between the different molecular components.

FIRST PART

EXPERIMENTAL DATA AND PREVIOUS STUDIES

1. Definitions. Experimental data.

If one were to give a genetic definition of three-dimensional polymers, one would have to say that they are derived from the polymerization of monomers, part of which at least is multifunctional, i.e., has a functionality equal to at least three. The term polymerization should be taken here in its widest sense, and should include polycondensation or polyaddition in the strict chemical sense [1]. Such a definition enables us to distinguish three-dimensional polymers from the linear polymers derived from the polymerization of exclusively bifunctional monomers. It shows immediately the importance of functionality, a generalization of the old concept of valence, which should be regarded as the number of chemical combinations of a certain (primary, for instance) into which a monomer may enter under adequate chemical reaction conditions.

From the experimental point of view, the behavior in the course of synthesis (polymerization, polycondensation, etc.) and particularly the rheological behavior of the two classes of polymers defined above is quite different. While the viscosity of bifunctional systems grows rapidly as a function of the degree of advancement p of the reaction, leading to fusible polymers (thermoplastic) soluble in appropriate solvents, the viscosity of multifunctional systems, nearing a certain value of the degree of advancement of the reaction known as the critical value, increases almost hyperbolically to become quickly, even sharply, infinite at the same value (Figure 1).

At experimental temperatures which may on occasion reach more than 200° C, the medium assumes the aspect of a mass which on the macroscopic level lacks all flow properties and resembles a jelly.

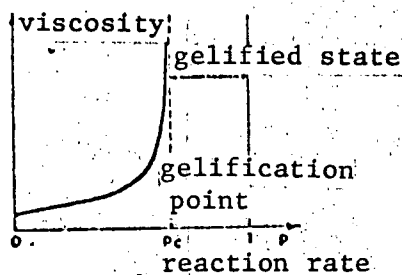


Figure 1. Rheological behavior of a multifunctional polymer during synthesis.

Gelification is said to occur.

The critical value of the reaction degree of advancement is therefore often referred to as the point of gelification or gel point.

2. Classical theories. Applications.

The detection of such a phenomenon provides a clue to the importance of the role of functionality. From the theoretical point of view, Carother [2] was the first to propose a simple relation permitting the calculation of the critical value of the degree of advancement of the reaction. He states that gelification occurs when — no other intermolecular connection being possible — the macromolecular compound is made up of a giant molecule. The gelification point is then found from the general Formula (1) for an infinitely large degree of polymerization:

$$p = \frac{2}{f} \left(1 - \frac{1}{\overline{DP}_n} \right) \quad (1)$$

$$p_c = \frac{2}{f} \quad (2)$$

In these relations, f is the average functionality of the system if it contains monomers of different functionalities. Thus, for a system made up of two moles of glycerol and three moles of phthalic anhydride with an average functionality of $f = 2.4$, Relation (2) yields a theoretical value of $p_c = 0.833$, on the order of the experimental values determined for various diacids [3, 5, 6, 7] and especially 0.796 in the present case [4].

Later, Flory [8-12], on the basis of statistical considerations, established a set of relationships which enable us to find the critical value p_c , the distribution of average molecular masses and the arrangement of soluble, gelified fractions for a certain number of macromolecular systems.

The theory is based chiefly on the following two hypotheses:

1. All functional groupings are equally reactive.
2. Any intramolecular reaction leading to cyclical structures is assumed not to occur.

These two hypotheses are corroborated by a number of experimental observations. Thus, Flory [13, 14, 15] showed for linear polymers that the reactivity of functional groupings did not depend on their size, at least if the first stage of the reaction was disregarded, and likewise the final stage as was shown later [16]. Moreover, Kienle [4-6] and Bradley [17, 18] showed for certain multifunctional polymers that, in the stages preceding gelification, the formation of intramolecular bonds was negligible.

The important parameter in Flory's theory is the "branching coefficient" α defined as the probability of a reactive group belonging to a multifunctional unit leading, by means of a chain of bifunctional units, to another multifunctional unit. The physico-chemical criterion for the occurrence of gelification is still the existence of infinitely large molecules whose dimensions would be, one way or another, on the order of those of the reaction recipient. The almost certain existence of such a lattice, therefore, determines the critical value of α :

$$\alpha_c = \frac{1}{f-1} \quad (3)$$

an expression in which f is no longer the average functionality, but the functionality of the branching units.

In the case of polycondensation which includes, for instance, bifunctional and trifunctional units of type A and bifunctional B units liable to interact, the computation of α as a function of p leads to the expression:

$$\alpha = rp_A^2p/[1 - rp_A^2(1 - p)] \quad (4)$$

where r : ratio of number of functional groupings of type A to number of functional groupings of type B.
 ρ : proportion of A groupings belonging to branching units.
 p_A : probability of an A grouping having reacted.

For the preceding stoichiometric phthalic anhydride-glycerol system, the functionality is $f = 3$. The relations above lead to a theoretical critical value of $p_c = 0.707$. For the adipic acid-pentaerythritol system, also stoichiometric, whose critical value determined experimentally is approximately 0.63 [19] to 0.65 [21], calculations yield a slightly lower critical value of $p_c = 0.577$. For more complex systems, such as mixtures of diacids, triacids, and dialcohols in variable proportions, the calculated values are still lower than the experimental values [8], while under the same conditions one can easily show that the values calculated from Carother's Relation (2) would be greater.

According to Flory, the discrepancy arises from the fact that the theory does not take into account, according to the second hypothesis, the possible intramolecular reactions. It was thought that this point of view could be corroborated by carrying out polycondensation in such a way as to eliminate intramolecular reactions. For that purpose, Stockmayer and Weill [20] measured the gelification points of the adipic acid-pentaerythritol system in solution in an inert solvent, first at low concentrations where the formation of cycles would be significant, and then at increasing concentrations, and finally, extrapolated from the preceding results at "infinite" concentrations (zero volume) where any possibility of forming intramolecular bonds would be eliminated. Under these conditions, obtaining a value of

$$p_c = 0.578 \pm 0.005$$

corroborated by similar experiments in different systems [22] appears to constitute a certain confirmation of the theory.

This theory also enables us to find the distribution of average molecular quantities, but only in the case of systems including

trifunctional units or tetrafunctional systems with a lengthwise distribution of uniform chains. Thus, it was generalized for systems including multifunctional units and lengthwise distributions of any kind of chain by Stockmayer [23, 24]. The criterion for the occurrence of gelification is confirmed, but the complexity of the expressions yielding the average molecular masses makes their practical use very awkward.

The problem of the formation of cyclical structures, on which the legitimacy of the preceding theories depends to a considerable degree, has given rise to numerous studies dealing with both the possibility of cyclization of linear polymers such as decamethylene-diol polyadipate [25] or multifunctional polymers from both a theoretical [26, 27] and experimental [28, 29, 30] point of view. The study of polyesters and polyalkoxysilanes in solutions showed that an increase in the value of the gelification point with a reduction in average functionality and increased dilution could even lead to the suppression of the gelification phenomenon. Polymers with rigid molecular chains, however, appear to depend less on the effects of dilution [29].

Initially established by taking the polycondensation process as a model, the original theories were quickly extended to the process of vinyl type polymerization by Stockmayer [24]. He shows, with the special example of vinyl-divinyl copolymers, that it is possible under certain conditions to interpret the general behavior of these systems [33] by assuming that the polymerization reactions in linear chains and bridging are not concomitant [31, 32], but consecutive.

However, experimentation shows that the interpretation of the polymerization process by the classical theory may well lead to serious miscalculations. Thus, Walling [34], in making a study of the gelification of glycol methyl-dimethacrylate methacrylate or vinyl vinyl-diadipate acetate in solution was able to observe gelification points quite different from the calculated ones. Only systems including bifunctional units in proportions of less than 0.2% could be regarded as giving experimental values in reasonable agreement

with the theory. It appears that the cause of this discrepancy must be sought in the special nature of the polymerization mechanism involving propagation rates much greater than diffusion rates [34], and probably also in the effects of dilution [30]. Comparable difficulties were likewise encountered in the interpretation of the behavior of diallyl polyphthalates, abundantly studied by Simpson [35-38]. Nevertheless, Gordon [40, 41] refutes the effects of diffusion on the delay occasioned by gelification, and invokes instead either the presence of a chain transfer reaction [40] or the formation of cycles involving the tendency of acrylic or allylic groupings with a like motif to be incorporated into the linear chain [36, 39, 40] or else the formation of multiple bridgings [38]. Nevertheless, Gordon [42] showed that, to the extent that intra-chain secondary polymerization reactions are known, the classical theory may be used, since the chain transfer reactions and multiple bridgings have only a negligible effect on the general development of the process.

In spite of the existence of later works [43, 44], a certain number of points still remain unexplained. Particularly, it is poorly understood why the three diallylic phthalates have similar gelification points, while the ortho-isomer exhibits a decided tendency toward intra-chain polymerization [45].

All of these difficulties appear enough to justify the trend toward theoretical and experimental studies aimed at perfecting the classical theory to be oriented toward the study of polycondensable systems instead. Thus, the principal modifications of the theory, whose purpose it was to reduce the fundamental hypotheses, dealt with such systems.

Thus, the behavior of systems with a certain category of similar functional groupings, but with different reactivities, was examined from a general point of view [46, 50] or for the purpose of making statistical models of macromolecules of natural origin [51]. The distribution of functional groupings according to their nature at the monomer level was also examined [52], as well as the effects of monofunctional monomers ultimately endowed with their own reactivity [53].

In a general way, the gelification theory was applied to a number of multifunctional polycondensable or polymerizable systems in order to justify — or to anticipate — the three-dimensional structure to which, not only gelification, but also reticulation and vulcanization are related. In this regard, we shall mention the elastomers [54, 55], certain types of polyamides [56, 57], phenol, polymerizable resin oils [58], thermally polymerizable oils [59, 60, 61], polyepoxide compounds [62, 63] and the formophenol system which provided the occasion for a new theoretical discussion [64].

It was extended to the study of the behavior of multifunctional macromolecular systems of mineral [65, 66] and natural [67] origin, particularly to the interpretation of certain transitory combinations of living substances such as the antigen-antibody system [68, 72].

3. Modern theories.

A statistical study of multifunctional polymers was taken up recently by Gordon [73]. It was based on new mathematical bases from the studies of Good [74, 75] carried out in the more general framework of the "theory of processes in a series" [76].

One of the most attractive aspects of Gordon's developments is that the use of generating functions permits us to calculate the different average molecular masses from the gelification point and the soluble fraction much more directly than by the use of the calculus of probabilities. It also enables us, in the special case of the adipic acid-glycerol case, to take into consideration the partial or complete elimination of the water produced by polycondensation as well as the effects of the different esterification rates of the primary and secondary hydroxyls. The preceding factors were generalized to cover "non-random" polycondensation, i.e., to the case where the formation of chemical bonds is affected by the already existing bonds in the molecules. It is valid to assume that its influence is linear, with good approximation — in other words, the free energy of bond formation is proportional to the number of bonds already established and born only by the first contracting patterns. Thus, we speak of a

"first-shell substitution effect". On this effect will depend the respective rates of formation and breaking of bonds, i.e., the equilibrium constant of the polycondensation reaction. Thus, the author computes for the two extreme cases, using the generating function of bond distribution, the average molecular masses, the gelification point, and the soluble fraction [77].

This theory was applied to the statistical description of the chain conformations of highly ramified polymers [78], to the calculation of the statistical parameters of the theory of rubber elasticity [79], and quite recently to the process of competitive formation of linear and cyclical structures in polymerization [80].

Still more recently, Whittle [81] examines the question from a primarily mathematical point of view as a general process of an aggregation of entities bearing "sites" between which bonds can be established. At first, he considers systems made of a single variety of units, all of whose sites are equally reactive. He gives a complete description of the aggregation process through the use of a generating function of the distribution of different types of aggregates. Later, he extends the preceding results to the case of systems made up of different units containing nonequivalent sites. Acknowledging that the bonding energy of a unit depends only on the number and nature of the units to which it is connected, the generating function (established from considerations of combinatory analysis) may be advantageously replaced by a system of partial differential, nonlinear, first-order equations established as a function of the equilibrium conditions. Then, by removing the interdiction of producing cyclical structures, we finish with a simplification, since the preceding differential equation becomes linear [82].

However attractive it may be as a result of its wide generality, it is unfortunately difficult to state that this last theory can, in the immediate future, be of any practical use.

4. Preliminary considerations.

The development of classical theories is characterized by a tendency toward generalization aimed at the progressive suppression of the multiple aspects of the two basic simplifying hypotheses and, consequently, by the construction of mathematical models ever closer to real models. If, in this regard, the hypothesis of equiprobability of producing bonds between sites (equireactivity of chemical functions) is no longer indicated because of the difficulty of theoretical treatment. On the other hand, the hypothesis which assumes the absence of lattice cyclization has long been retained. Moreover, in its modern form, it is implicitly contained in the concept of processes in a series whose corresponding type-diagram (graph) belongs to the family of topological trees (Figure 2). Only recently, as we have just seen, have certain authors been able to conceive of the possible existence of cycles by suitable modifications of the description of a process in series.

If it were not questionable that the structure conditions all the properties of multifunctional macromolecular compounds, the special structure derived from the possibility of cyclization would likewise have to contribute to the interpretation of these properties, one of the principal phenomenological aspects of which is gelification. This contribution would have to permit us to make up the differential observed between the gel points calculated from classical theories and those found experimentally by massive polycondensation of multifunctional macromolecular systems.

In the following presentation, we concede, for the purpose of simplification, as a starting hypothesis (subject to later revision, as seen later) the equiprobability of producing the chemical bonds which are possible between reactive sites both in time and space. On the other hand, we shall not formulate a priori any hypothesis assuming the exclusion of any possibility of cycle formation. We shall make this notion more specific as the discussion proceeds by referring both to experimental considerations in the framework of chemical data.

and theoretical considerations in the framework of the axiomatic theory of graphs.

The description of the evolution of infinite random graphs has already been taken up from an essentially mathematical standpoint by Erdos and Renyi [83]. Their application to a number of real processes pertaining to the fields of physics, chemistry, biology, industry, and telecommunications led Hammersly [84] to distinguish, on the one hand, processes of diffusion, and, on the other hand, processes of percolation, of which the telecommunication, contamination, and particularly the multifunctional polymer gelification are special cases.

As a physical chemist, I propose to discuss the latter case for finite multifunctional macromolecular systems. Such systems, made up of a finite and known number of elements, will exhibit a known, finite maximum number of bonds which are chemically achievable by the consummation of suitable pairs of suitable sites. The state of a system can then be described in terms of a quantity p (rate of reaction advancement) which, in the direction of evolution corresponding to synthesis (polymerization), will be equal to the ratio of the number of actual bonds to the number of possible bonds. This ratio, a date in the evolution of the system, varies discretely between two extreme values, zero and one, corresponding to two similarly extreme states: a state I characterized by the lack of bonds (set of disjointed monomers) and a state S characterized by the presence of a number of bonds equal to the maximum number of possible bonds. In the form $d = 1 - p$, it is the rate of development of the system in the inverse sense from the preceding (rate of degradation).

To conceive of the most complete description possible, both from the topological and statistical standpoints, we shall assume that the development takes place in both directions according to a succession of semisteady equilibrium states.

If, in view of certain hypotheses and constraints of experimental origin, we assume that the phenomenon observed as a function of p

corresponds to the most probable occurrence of the random process, we can speak of the stochastic description of amphidromous systems [85].

SECOND PART

TOPOLOGICAL DESCRIPTION

Here we propose to examine the lattice structure of a multifunctional macromolecular system developing in a random fashion. At any moment in its development, we are interested solely in the properties which remain invariable in the course of the possible structural transformations, that is, only the topological properties. At first, we shall consider an ideal lattice characterized by an almost total lack of constraints, particularly those of spatial origin, and, consequently, all of the steric conformations which are equally possible. Next, progressively, to conclude with a theoretical model of real systems, we shall introduce into the ideal lattice a certain number of constraints derived from experimental considerations.

1. Schematic representation.

Schematic representation of a macromolecular lattice, and especially of a lattice in a gelified state, must refer to two different models, one of which may be termed the theoretical model and the other, the chemical model.

1.1. Theoretical model. It was first proposed by Flory [8]. We have represented the multifunctional units ($f = 3$) by points (Figure 2a). The straight lines represent the molecule portions of a certain length made up of bifunctional units ("chains") and included either between two "branching units" or between a branching unit and a bifunctional unit, one of whose extremities has not reacted. The extremities of the "chains" are situated successively on concentric circles centered on the middle of an original "chain" selected arbitrarily. Every "chain" extremity, made up of one branching unit, produced two — more generally ($f - 1$) — new "chains" whose

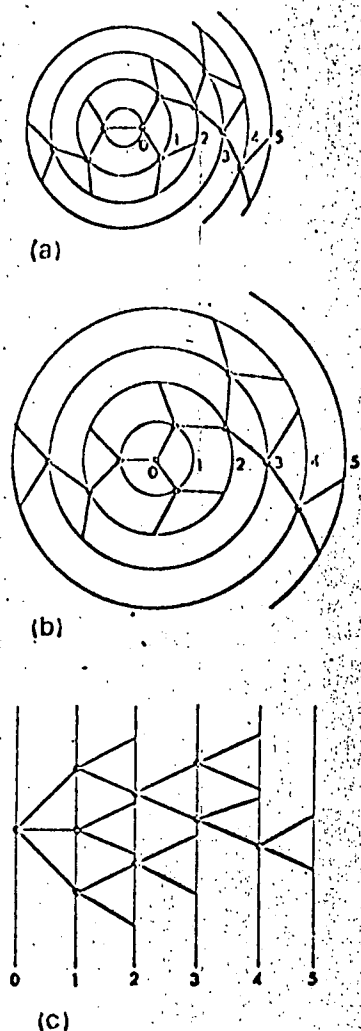


Figure 2. Schematic representation of a topological tree.

- (a) Flory's theoretical macromolecular model [8].
- (b) Model derived from (a).
- (c) Model derived from (b). Process in a series or "family tree" type.

extremities in turn have the same capability. Circles (Figure 2b) with their center at a branching unit arbitrarily selected as the origin and numbered 1, 2, 3 etc., form the geometrical locus of the possible points of departure of multiple generations succeeding each other away from the origin. The transformation of the concentric circles into parallel lines leads to the customary schematic representation (Figure 2c) of a process in a series [73], an important example of which is a family tree. This representation answers the definition of a topological tree: between two points of a tree there exists one and only one chain.

It should be noted that the bifunctional units not represented here and not liable to multiple descendance must be regarded as simple generations which do not play a part in the continuity of the process, except to give the "chains" variable lengths without any structural effects.

The schematic representation of macromolecules with a tree structure can consist of a set of points arranged at random, representing the multifunctional units, and curved lines indicating the possible conformations of the chains (Figure 3a, 3b).

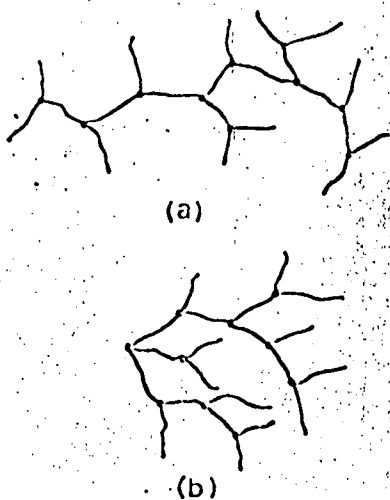


Figure 3. Schematic representations of two possible conformations of a multifunctional macromolecule with "tree" structure.

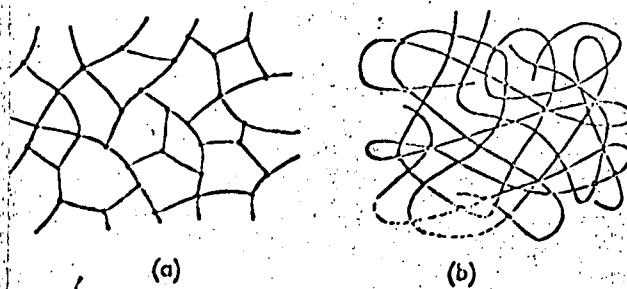


Figure 4. Schematic representations of two possible structure types for a multifunctional macromolecule without tree structure (chemical model).

1.2. Chemical model. This is the model generally adopted by writers dealing with the structure of multifunctional macromolecular compounds from a more specifically practical standpoint. It shows two views of different complexity (Figure 4a, 4b). In contrast to the previous model, it is characterized by the fact that between two points of the lattice there may be more than one chain going from one to the other. Nevertheless, in view of this possibility, two types of structure may appear: either it is possible, by elastic deformation of the lattice, to give a representation in a plane without the two chains intersecting, except for their multifunctional extremities (a), or else such a representation is not possible (b).

To the extent that the synthesis of the lattice occurs from monomers immersed at random in a three-dimensional space, a structure of type (a) can be obtained only if the random generation conditions of the lattice include certain supplementary constraints. These constraints require that a subset of monomers and their bonds be located on a surface homeomorphic with a plane which thus constitutes

a sheet molecule (lamellar). If macromolecules of this type exist in nature, it does not appear that synthesis would have succeeded in bringing into play the constraints necessary to obtain them⁽¹⁾. Thus, in the absence of special constraints and in view of our hypothesis (which is most probable in the general case) of spatial equireactivity, we are led to consider structure (b) as most typical of the gelified state.

2. Elements of the theory of graphs.

A comparative study of the typical values of the preceding graphs on a rational basis is possible if we note that they belong strictly to graphs according to the definition first given by D. Konig [86].

The theory of graphs was applied very early to organic chemistry by G. Polya [87] and then by T. L. Hill [88], but appears to have been taken up again only much later [89]. Quite recently, Van Wazer and his colleagues make use of it in the study of random exchange reactions for radicals in mineral and organic macromolecular compounds [90].

From a chemical standpoint, a polymer must be regarded as a set of monomers endowed with chemical reactivity, among which chemical reaction R creates a correspondence which is manifested as the occurrence of bonds whose number depends on the rate of advancement of the reaction. For a given rate of advancement, a polymer is thus comparable to a set M of monomers and a set A of bonds involving a set of pairs of M . The chemical reaction R produces a partition of the set of monomer molecules. The latter is formed of disjointed sets of monomers connected to one another, which comprise the molecules of the polymer.

From an axiomatic point of view [91], we shall say that the chemical reaction is a mapping of M on M . However, starting with:

(1) M. L. Huggins has synthesized macromolecular compounds with foliated structure [118].

- a set M ,
- a mapping R of M on M ,

we have a graph $G = (M, R)$ made up of the set M and mapping R . The mapping R will be manifested on the graph by a set A of continuous lines joining pairs of points (m_i, m_j) such that: $m_i \in M, m_j \in M$.

The points or vertices m_i , elements of M , represent the monomers. The set of continuous lines completely determines the mapping of the graph just as mapping R determines set A . Therefore, we can write the graph either in the form $G = (M, R)$ or $G = (M, A)$.

A bond, once established between two monomers by means of the reactive sites which they bear, makes these two sites correspond on a one-to-one basis. If two sites are always connected by two lines in opposite directions, the graph is symmetrical. For simplicity, we can connect the two vertices by a continuous line with no direction indicated, designated as a "cross-link".

2.1. Terminology. The terminology of graph theory, created by mathematicians [91], is quite closely related to that used customarily in macromolecular chemistry. Thus, we propose to adopt the terminology of graph theory, both for generalization and for precision, to be supplemented where necessary by terms of chemical origin to the extent that these terms will fill a void in current mathematical language for the physical chemist.

1. Thus, the degree of a vertex m_i is the number of cross-links with one extremity at m_i , and the other different from m_i .

We shall generalize this definition and use the functionality f of a vertex m_i for the number of sites it contains, each vertex being given in advance as the collection of a certain number f of sites. The extremities of every cross-link occupy two sites (ultimately belonging to the same vertex) and one site capable of receiving only one cross-link.

Functionality is the maximum degree a vertex may have. It is generally determined in advance. For a monomer, it is the number of functional groupings it possesses which can react under physico-chemical reaction conditions.

Node refers to any vertex having a degree equal to or greater than three, and antinode refers to any other vertex. We shall use a rather different definition, using node for any vertex with a functionality equal to or greater than three, and antinode for any vertex with a functionality equal to two. It follows that, in view of the evolving character of the graphs envisaged, any node or antinode with a degree lower than its functionality may be regarded as a pre-node or a pre-antinode, respectively, because of its capability of becoming a node or an antinode in a graph in the sense of graph theory [91].

2. A chain is a sequence of cross-links, each cross-link attached to the preceding cross-link by one extremity and the succeeding cross-link by the other extremity.

A linear chain will refer to a chain for which all vertices are antinodes, and a ramified chain will refer to a chain, part or all of which is made up of nodes.

A branch will indicate a linear chain for which only the extremities belong to nodes.

3. A vertex is called terminal when it has only one incident cross-link. We shall say that a cross-link or a linear chain or a branch is terminal when it ends in a terminal antinode.

By extension, a cross-link or a linear chain whose two extremities are antinodes will be called floating.

An isolated vertex is one with no incident cross-link.

4. A cycle is a finite chain beginning from one vertex and finishing at the same vertex. It is called elementary if all the vertices are different.

The length of a chain is the number of cross-links in the sequence. A cycle of unit length, made up of a single vertex and a single cross-link, is a loop.

5. A graph is connected if, for every distinct pair of vertices, there is a chain going from one to the other.

A subgraph of $G = (M, R)$ is by definition a graph with the formula $G = (N, R_A)$ such that:

$$N \subset M \text{ and } R_{Am_i} = Rm_i \cap N, \forall m_i.$$

A subgraph (M, A_N) will be made up of a set of vertices $N \subset M$, and a set of cross-links of A_N joining two vertices of N .

A partial graph of $G = (M, R)$ is by definition a graph $G = (M, R_p)$ such that:

$$R_p m_i \subset Rm_i, \forall m_i.$$

A partial graph (M, A_p) will be made up of all vertices M , and all cross-links of a set $A_p \subset A$.

A partial subgraph is a partial graph of a subgraph.

A connected component (or component) of a graph is a connected subgraph of the graph. It follows that:

— the different connected components of a graph $G = (M, A)$ constitute a partition of M . There is a close correlation between the terms components of the graph and molecules of the macromolecular system:

— a graph is connected if, and only if, it has only one component.

A multigraph $G = (M, A)$ is a graph for which there may be several distinct cross-links joining the same pair of vertices.

A graph or a multigraph G is planar if it is possible to represent it on a plane in such a way that the vertices are distinct points, and two branches meet nowhere but at their extremities. The representation of G in a plane, in conformity with the conditions required, is called a topological planar graph. Two topological planar graphs which can be made to coincide by elastic deformation of the plane are regarded as identical.

Generally, any graph G can be represented in three-dimensional space with no two branches intersecting. Such a representation is called a topological graph. If S designates a surface of three-dimensional space, and if there is biunique and bicontinuous mapping σ of G on S , we know that two cross-links of σG will not intersect. σG by definition is an S -topological graph. If S is a plane, we again encounter the concept of a topological planar graph.

It follows from the general theorems [92] that any finite graph can be represented on an orientable surface S of type g (homeomorphic with a surface delimiting a volume pierced by g holes), where g is sufficiently large. If g is zero (case of a sphere) we return to a topological planar graph for a finite graph G .

The representation of a topological graph S by projection on a plane will cause the cross-links to intersect. These must not be confused with the nodes, which should be denoted in an appropriate manner (Figure 4b).

In the field of elastic deformation corresponding to the states of maximum coiling and complete extension of macromolecular chains, the different conformations of a polymer will constitute a topological graph.

2.2. Basic theorems. Let us consider a multigraph G with m vertices, a cross-links, and c connected components. Let us set:

$$\begin{aligned} \rho &= m - c \\ v &= a - \rho \end{aligned}$$

whence

$$v = a - m + c \quad (5)$$

By definition, v is the cyclomatic number of multigraph G . It is the Betti number for the dimension of the variety considered, i.e., for a graph.

ρ is called the cocyclomatic number.

Formula (5) is a special form of the Euler-Poincaré relation [93] for a graph which is not necessarily connected.

Theorem I. Let G be a multigraph and G' a multigraph with $(a + 1)$ cross-links obtained from the preceding ones by joining two sites s_i and s_j of G with a new cross-link:

1. If s_i and s_j do not belong to the same vertex, or if (when s_i and s_j belong to two distinct vertices) these two vertices are not connected by a chain in G , we have:

$$\begin{aligned} \rho' &= \rho + 1 & v' &= v \\ c' &= c - 1. \end{aligned}$$

2. In the opposite case, we have:

$$\begin{aligned} \rho' &= \rho & v' &= v + 1. \\ c' &= c \end{aligned}$$

Corollary. We find: $\rho \geq 0, c \geq 1, v \geq 0$.

Theorem II. The cyclomatic number v of a multigraph is equal to the number of linearly independent elementary cycles.

This means that v is also the dimension of a cycle base, that is to say, the dimension of a vector subspace produced by the cycles,

so that every other elementary cycle depends on it linearly [94]. It follows that a set of cycles will be made up of independent elementary cycles if each of them contains a cross-link not contained by the others.

Corollary I. A graph has no cycles if, and only if, $v = 0$.

Corollary II. A graph may have a cycle if, and only if, $v = 1$.

3. Evolving random graphs.

The concept of an evolving graph proceeds directly from the evolving chemical nature of the macromolecular systems considered here. The evolution of these finite systems occurs within a field, which is itself well-defined. In fact, if we may say generally that the number m of elements in set M of the monomers is invariable in time, i.e., in the course of a chemical reaction, there is no loss of monomers from the reaction medium — either through evaporation, sublimation, distillation, or through secondary chemical transformation. On the other hand, the number a of bonds varies in the course of time, in a fashion directly proportional to the rate of evolution values between zero and one.

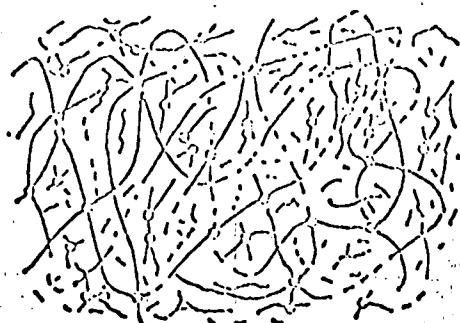
At every moment of evolution, in the sense that we shall adopt henceforth and which will be that of the polymer synthesis, the graph of the system is a partial graph $G = (M, R_p)$ of graph $G = (M, R_1)$ of the system in its saturated state S corresponding to the limit of its evolution ($p = 1$).

The chemical evolution of the system may thus be described by a succession of partial graphs $G = (M, R_p)$ corresponding to the set of discretely increasing values of p such that: $0 \leq p \leq 1$. Graph $G = [M, R(p)]$ will be termed evolving. 280

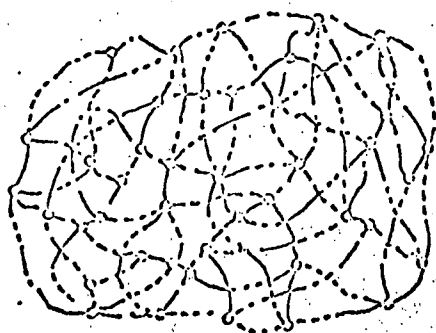
Given the random nature of the mapping $(R(p))$, the system can be represented by any one of the graphs of class \mathcal{G} including the set of graphs whose characteristic numbers v , a , m and c satisfy the

Euler-Poincaré relation, in which m is given in advance, and a depends on the moment of evolution considered. It follows that, if the values of v or of c can be determined, it will be possible to know at least one certain aspect of its structure.

We can say that the graphs are statistically identical if their characteristic numbers are equal. Under these conditions, class \mathcal{S} of these graphs can be represented conventionally by producing one of them which will be designated the statistical graph or average graph.



Real graph G



Support graph Z

Figure 5. Support graph associated with real graph (2).

The study of the topological structure of the graph of an evolving random macromolecular system can be reduced conveniently in the first approximation to a study of class \mathcal{S} of statistical evolving graphs whose characteristic numbers at any moment satisfy the Euler-Poincaré relation in which m is given in advance.

3.1. Graph of an ideal system.

3.1.1. Definitions. Let us recall that by ideal system we mean any system in which actual bonds between two functional groupings are subject to no topological or metrical constraint.

Vertices. We assume, as in the following, that there are no vertices with only a single site.

(2) The gaps in graph Z correspond statistically to nonrealized or nonrealizable cross-links in graph G at a date p in its evolution.

The functionality of the vertices will be either equal to, or greater than, two. The number of vertices with functionality f will be designated by m_f , and the average functionality of all vertices of the graph — by \bar{f} .

Cross-links. Every cross-link occupies two arbitrary sites. We assume for convenience that the number of sites is even. The maximum number a_1 of cross-links which the graph can support at saturation will be equal to the number of pairs of sites.

If a graph $G = (M, A_p)$ has a cross-links, we say that it has $(a_1 - a)$ pre-cross-links which can become cross-links in a later realization of the graph.

Support graph. We shall use the support graph to indicate a graph $\Sigma = (M, A')$ from which any graph $G = (M, A_p)$ can be obtained by the suitable suppression of cross-links (Figure 5). For an ideal system, it is identical with the saturated graph $G = (M, A_1)$.

Rate of evolution. This is expressed as:

$$p = \frac{a}{a_1} = \frac{2a}{\bar{f} \sum_f m_f} \quad (6)$$

Its different values are whole multiples of the discrete quantity: $2/\bar{f} \sum_f m_f$.

3.1.2. Structural state equation. The structural state of a system will be assumed sufficiently known if — when the number of vertices and their functionality are given in advance — the characteristic numbers of the average graph which satisfy Formula (5) are known. By expressing the number of cross-links as a function of the rate of evolution, (5) yields the structural state equation of the evolving graph:

$$v = p \frac{\bar{f}}{2} \sum_f m_f - \sum_f m_f + c \quad (7)$$

$$v = \sum_f m_f \left(p \frac{l}{2} - 1 \right) + c \quad (8)$$

This relationship has a linear form. It represents a plane σ in three-dimensional space with reference axes $(O\vec{v}, O\vec{c}, O\vec{p})$. This plane is parallel to the bisector of angle $(O\vec{v}, O\vec{c})$. The limits of variation of parameters v, c, p determine a field in this plane inside which any point represents the state of the graph (Figure 6)⁽³⁾.

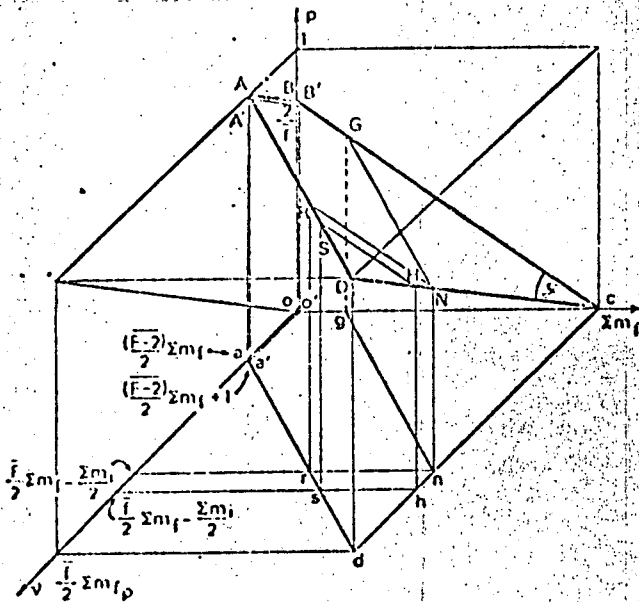


Figure 6. Structural state domain of a multifunctional ideal graph.

3.1.3. Structural state domain. It depends generally on a certain number of constraints inherent in the system, which have to do with the conditions under which the cross-links are produced. In the case of an ideal system, the only constraint to be considered is that of the distribution of a well-defined number of sites f at each of the vertices.

3.1.3.1. Constraints inherent in the system. It determines a polygonal contour whose vertices have the following coordinates:

$$\begin{array}{l} C \left\{ \begin{array}{l} v = 0 \\ c = \sum_f m_f \\ p = 0 \end{array} \right. \quad B' \left\{ \begin{array}{l} v = 0 \\ c = 1 \\ p = \frac{2}{l} - \frac{2}{l \sum_f m_f} \end{array} \right. \quad A' \left\{ \begin{array}{l} v = \frac{(l-2)}{2} \sum_f m_f + 1 \\ c = 1 \\ p = 1 \end{array} \right.$$

⁽³⁾ For convenience in reading, the scale along $O\vec{p}$ has been multiplied by an arbitrary factor.

F designates the functionality of a node.

If the vertices all have even functionality:

$$D \left\{ \begin{array}{l} v = \frac{1}{2} \sum_f m_f \\ c = \sum_f m_f \\ p = 1. \end{array} \right. \quad (9)$$

The contour of the corresponding domain is: A'B'CD.

If a portion or all of the vertices has an odd functionality f_1 , the maximum value of v is:

$$v' = \frac{1}{2} \left(\sum_f m_f - \sum_{f_i} m_{f_i} \right). \quad (10)$$

The contour of the corresponding domain is: A'B'CHS.

3.1.3.2. Supplementary cyclization constraint. Here we shall introduce a supplementary constraint which, in connection with the study of real system, has a certain experimental justification. We assume that: no cycle, even one reduced to a loop, composed exclusively of antinodes, may exist. Under these conditions, the maximum value of v is:

$$\begin{aligned} v'' &= v' - m_i \\ v'' &= \frac{1}{2} \left(\sum_f m_f - \sum_{f_i} m_{f_i} \right) \end{aligned} \quad (11)$$

The contour is then A'B'CNR. It is restrained with respect to the preceding ones.

3.1.4. Reduced state equations. A comparison of evolving graphs of arbitrary size but with the same average functionality f (average isofunctional graphs) is possible using several reduced state equations obtained from the state Equation (7), if we define a certain number of average quantities.

1. Relation (7) can be written in the form:

$$\frac{c}{\sum f} - \frac{v}{\sum m_f} = 1 - p \frac{f}{2} \quad (12)$$

or:

$$\frac{1}{\overline{DP}} - \frac{1}{\overline{DPC}} = 1 - p \frac{f}{2} \quad (13)$$

$\overline{DP} = \sum \frac{m_f}{c}$ is the ratio of the vertex number (or points) of the graph to the number of its components. We shall refer to it as the average degree of punctuation. In a similar fashion, $\overline{DPC} = \sum \frac{m_f}{v}$ will be termed the average degree of cyclomatic punctuation. Obviously, this is meaningless, unless v is other than zero. If $v = 0$, we have Carothers classical relationship [1] which in macromolecular chemistry relates the numerical average degree of polymerization to the rate of advancement of the polymerization in the case of macromolecular systems without cycles. Let us note that \overline{DP} cannot be infinite in the mathematical sense of the term, but at the most equal to $\sum \frac{m_f}{c} (c=1)$.

If $p = 2/f$, then $v = c$. The system contains at least one cycle if it has only one macromolecular component.

2. Relationship (7) can be written in the form:

$$\frac{v}{c} = 1 - \frac{\sum m_f}{c} \left(1 - p \frac{f}{2}\right) \quad (14)$$

$$\overline{DC} = 1 - \overline{DP} \left(1 - p \frac{f}{2}\right) \quad (15)$$

$\overline{DC} = \frac{v}{c}$ is the ratio of the number of linearly independent cycles of the graph to the number of its components. We shall term it the average degree of cyclization (or cyclomatic degree).

The following theorem follows from that relationship:

Theorem III. Let there be an evolving multifunctional graph whose average functionality of the vertices is f and the rate of evolution p :

If $p < \frac{2}{f}$: the graph may not have linearly independent cycles.

If $p = \frac{2}{f}$: the graph is necessarily cyclical, and has a cycle if it is connected. If it is not connected, and if it contains c components, it will have $v = c$ linearly independent cycles.

If $p > \frac{2}{f}$: the graph must necessarily have a cycle base.

Relationship (7) may also be written in the form:

$$\frac{v}{c} = \frac{p \frac{f}{2} \sum m_f}{c} - \frac{\sum m_f}{c} + 1 \quad (16)$$

or:

$$\overline{DC} = \overline{DL} - \overline{DP} + 1 \quad (17)$$

which would enable us to define $\overline{DL} = p \frac{f}{2} \sum m_f / c = a/c$ as the average degree of bonding (or ligamatic degree). Let us note that \overline{DL} and \overline{DP} are rigorously equal only if $\overline{DC} = 1$, i.e., if $p = 2/f$.

3. We could likewise have defined the average cyclomatic degree of bonding $\overline{DC} = a/v$, which obviously is meaningless unless $v \neq 0$.

3.2. Linear and cyclomatic complexes. Let us consider the set \mathcal{G} of graphs of a multifunctional macromolecular system defined by the number and functionality of the different vertices, whose

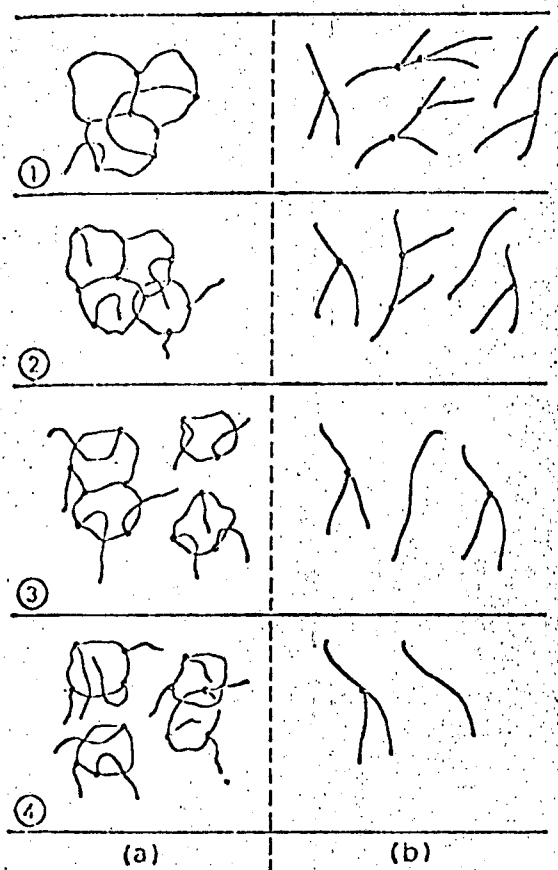


Figure 7. Example of isocyclo-evolutive complexes of a graph $G = (M, R_p)$ (p and v constants $\Rightarrow c = Ctc$).

- (a) Cyclomatic complexes, non-planar (1, 2, 4), planar (3).
 (b) Line complexes.

$T_1, T_2 \dots$ It is possible to arrange by type, in one and only one way, the components of a graph $g \in \mathcal{G}$. Such an "arrangement" is called a complex.

We shall use the term linear complex of g to designate the restriction of the complex to the set of types corresponding to the cycleless components (or linear components: trees, floating linear chains, isolated vertices). In a similar manner, we shall call a cyclomatic complex of g , the restriction of the complex to the set of types corresponding to cyclic components.

The set of complexes of graphs of a class \mathcal{G} of statistical graphs, for which, in addition to the functionality and the number of vertices, the rate of evolution and the cyclomatic number are given, will constitute a set of isocyclo-evolving complexes (Figure 7). Let us note that, in the case where class \mathcal{G} is reduced

to a connected graph whose set M of vertices is small, we return to the classical concepts in general chemistry of isomerism, tautomerism (set of desmotropic forms), mesomerism [95] or resonance [96], depending on whether we consider these complexes successively or more or less simultaneously.

The ensemble of complexes of graphs in different classes & of statistical graphs constitutes an ensemble of cyclo-isoevolutive complexes (Figure 8) for which the cyclomatic number takes on all permissible values which satisfy the equation of the structural state, for a fixed rate of growth.

At a given point p of growth, these two ensembles of complexes constitute the amount of various chain-cycle equilibrium states which are topologically possible, which introduces the important concept of trans-reaction.

3.3. Graph of a Real System.

3.3.1. Additional Constraints. Compared with an ideal system, a real system can present and does present, in general, a certain number of additional constraints. Here we will only consider those which influence the nature of the points.

If bonds can be established, as in the case of an ideal system, between two arbitrary points which, from the point of view of the establishment of bonds can be considered identical, we say that the system is homogamic. If, on the other hand, bonds cannot be established exclusively between well determined pairs of points, then only those bonds can appear which are specific to the nature of the points from which they emanate.

Chemistry and even biology have numerous and important examples of such bonds. The specific characteristic is that there are systems which have points which, of necessity, belong to species which can be differentiated. Such systems will be called heterogamic.

3.3.2. Cyclisation Constraint. Experimental Justification.

This constraint is introduced for convenience in the study of a real system and can be justified to an acceptable degree of approximation in the study of the chemistry of real systems. In effect, whereas in chemistry there are examples of cyclical molecules, which

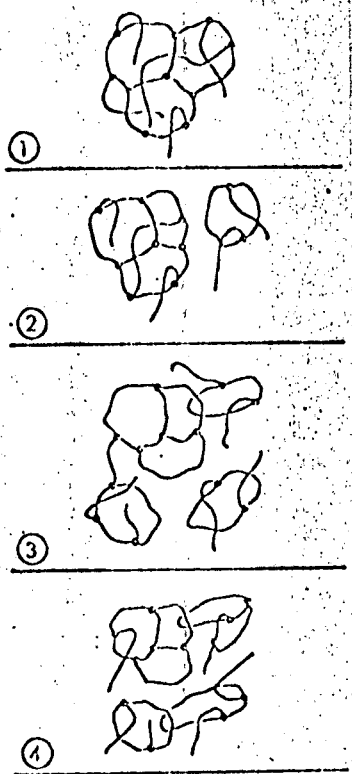


Figure 8. Example of cyclomatic cyclo-isoevolutive complexes of a graph $G = (M, R_p)$ ($p = \text{constant} \Rightarrow v - e = \text{constant}$).

polysiloxanes [103]. The existence of such oligomers conforms to the conditions of minimal internal stress of the cycle [102] or conditions of maximum stabilization of the structure by hydrogen bonds [100]. The proportion of these cyclical oligomers, which seems to depend on temperature, is generally small: it is on the order of 1 part per 100 [102] to 6 parts per 100 [104] with respect to weight.

The totality of these experimental data makes it possible to make our hypothesis of non-cyclisation of linear chains legitimate. On the other hand, we admit that there is a possibility of cyclization of branched chains, no matter what the number of nodes is.

The theoretical expression for this constraint in terms of the theory of graphs simply amounts to the statement that the supporting graph Σ , associated with the real graph, is connected.

only consist of bifunctional monomers, the number of repetition modes which participate in the cyclical structure is always small and the number of these oligomers is small in general in the system. Thus, for example, the number of repetition modes is on the order of 3, 5 or 6 for cyclo-oligo-hexamethylenediamines [97]. There are 1, 2 or 4 such repetitions for mono- and bi-cycloadipate of hexamethylenediamine [98] [99]. It has been possible to isolate cyclical dimers, trimers and tetramers of ϵ -caprolactame [100], cyclical monomers and dimers of adipate of decamethylenediamine [101]. It has also been possible to isolate cyclic trimers from polyterephthalate of glycol [102] or of the

3.3.3. Homogamic Graph. This is a graph of a macromolecular system for which the reacting points are free radical extremities, for example. For this reason, we will include in this category systems whose reactive functions are ethylene functions, or acetylene functions, by assimilating an ethylene function at a pair of reactive points. This gives a functionality equal to two to the monomer which supports it. In reality, the functionality will be a constraint which is inherent to the real system under consideration. Thus, an ethylene function will be bifunctional in the general case of vinyl derivatives. However, in certain cases, it must be considered as monofunctional ("dimerisation" of fatty ethylene acids). There is also the possibility that two double conjugate bonds must be considered as a bifunctional ensemble (a Diels and Alder type reaction).

This is the commonly used approach, but one should also consider the evolution of the system from the viewpoint of evolution of the ensemble of cyclomatic complexes of its multigraph. A double ethylene bond is considered as a cycle of the graph.

If we adopt the first point of view, the representation of a real graph at a certain point p of evolution will be obtained from the supporting graph Σ by suppressing a suitable number of cross-links, corresponding to the number of prior cross-links. A branch of the real graph (strictly speaking, a pre-branch) will consist of a branch from the supporting graph containing all the realizations corresponding to the pair of nodal points, to the anti-nodes, to the cross-links and the prior cross-links of this branch. Let B_i^k be a branch having k possible cross-links ($k - 1$ anti-nodes) and i pre-cross-links. We will say that this branch is of order i and has a ligamic number k .

3.3.4. Heterogamic Graph. In the following, heterogamic systems, which we will examine, will consist of points which only belong to two distinct types. We will consider systems in the polyester class and in the polyamide class, etc., and we will exclude their copolycondensates.

Let N_A and N_B , respectively, be the number of points in space A and B. We set:

$$r = \frac{N_A}{N_B} \quad (18)$$

When the stoichiometric ratio r is different from one, the supporting graph Σ consists of a certain number of cross-links which occupy identical pairs of points which belong to the major portion of space and cannot be realized in the real graph. We will call them anti-cross-links.

Let p_A and p_B , respectively, be the proportion of points A and B which are involved in an intersection of the real graph. We always have:

$$N_A p_A = N_B p_B$$

where:

$$r p_A = p_B \quad (19)$$

The number of cross-links of the real graph can only be at the most equal to the number of points which belong to the minor portion of space. The rate of evolution is expressed by:

$$\begin{array}{ll} p_A & \text{if } r < 1 \\ p_B & \text{if } r > 1. \end{array}$$

By generalized rate of evolution p , we mean the number of completed bonds to the number of bonds which can and cannot be realized. For the graph Σ , this is the ratio of the number of achieved cross-links to the total number of cross-links (cross-links, pre-cross-links, anti-cross-links), or the conversion rate of these pre-cross-links into cross-links, no matter what their type and taken with respect to all of these cross-links. We immediately find:

$$p = \frac{2r p_A}{r+1} = \frac{2p_B}{r+1} \quad (20)$$

The representation of a real graph at a certain point p in its evolution is obtained from the supporting graph Σ by suppressing the pre-cross-links and the anti-cross-links in a convenient way and in a random fashion.

The notion of generalized rate of evolution can remain completely general according to theorem III.

Let B_{ij}^k be a branch having: k cross-links which are possible and not possible ($k - 1$ anti-nodes, i pre-cross-links and j anti-cross-links). We say that this branch with ligamic number k is of order i and of anti-order j .

Even though we have already considered the parity of the point distribution with respect to the nodes, we must add the constraint regarding the nature of the point distribution in this case. It may be taken into account in a convenient fashion by first examining it at the level of the anti-nodes. This leads to consideration of the following two cases:

3.3.4.1. Pseudo-Heterogamic Graphs. For these graphs, the anti-nodes contain two points of different kinds: a point A and a point B .

It follows that if the stoichiometric ratio is different from one, the branches of the supporting graph Σ can only either be of anti-order zero, or anti-order one.

If the stoichiometric ratio is such that all the branches have anti-order one, the graph consists of an ensemble of branched components which all have one node. Polymers in the polyamide class have a network of this type ("star") and have already been examined [56].

3.3.4.2. True Heterogamic Graphs. For these graphs, the anti-nodes have two points which belong to the same space A or B . The anti-nodes A and the anti-nodes B can exist in any proportion.

Three different types of branches must be considered, depending on the type of nodal points: branches of type AA, AB or BB. Branches of the type AB are different from branches having identical extremities due to the parity of the number of anti-nodes which they can have in their saturated form. When the stoichiometric ratio is different from one, it is convenient for the study of the supporting graph to add to the system anti-nodes belonging to the minor portion of space, in a number which will satisfy the stoichiometry. These anti-nodes, which cannot be distinguished from the real anti-nodes of the system from the point of view of the random generation of the graph, but, nevertheless, measurable by an appropriate procedure will be called fictitious.

The supporting graph of this new system will be called fictitious supporting graph Σ' . A cross-link established between a real point and a fictitious point will be called fictitious. By suppressing fictitious anti-nodes and pairs of fictitious cross-links from the ensemble of the branches of the graph Σ' , the same number of anti-cross-links will be generated. In this way the supporting graph Σ of the real graph will be constructed whose branches can be of any arbitrary anti-order, in contrast to the pseudo-heterogamic graphs.

It follows from the preceding that we have been able to take into account the constraint regarding the distribution of the nature of the points, both for the anti-nodes, as well as for the nodes.

4. Axiomatic Definitions.

4.1. Intermolecular and Intramolecular Bonds. Bonds existing within a chemical system will be called intermolecular or intramolecular if the cross-links of its evolution graph have properties 1 and 2 of theorem I, respectively.

Stated differently, the creation of an intermolecular bond brings with it a reduction equal to the unit of the number of molecules of the system. However, the realization of an intramolecular bond keeps the number of molecules constant, but, ipso facto,

brings about a cycle which is linearly independent. This proposition is also true in the opposite sense when considering the evolution in the direction of degradation.

It follows from this definition that the intermolecular or intramolecular character is not necessarily an inherent property of the bond. It depends on a certain topological context.

Thus, a priori, all bonds which participate in the base of a cycle can be considered as intramolecular. However, we know that there exists only a certain number v , the suppression of which will make the components connected and without cycles. From this, it follows that all remaining bonds are intermolecular bonds.

On the other hand, we can say, a priori and for a given topological configuration, that all bonds which do not participate in a cycle base are intermolecular.

We should note that this definition, which has a topological origin, does not take into account the nature of the bonds which, in reality, can be differentiated according to their free energy of activation. Any definition, based primarily on the nature of the bond, and no matter how convenient it is in certain simple cases, will be no more arbitrary from the topological point of view and, therefore, could lead to misunderstandings.

4.2. Gelification. By gelification of a multifunctional macromolecular system, we mean the passage from a nongelified state to a gelified state.

The term degelification can designate the opposite process. No matter what the evolution direction, we will adapt the term critical transition.

The physical, physico-chemical and mechanical properties of multifunctional macromolecular systems, in either one of these two states, are sufficiently different to suggest that they depend

directly on the nature of the net. If we only examine the most representative properties: fusibility, viscosity, solubility, expansion, which are intimately connected to the relative mobility, or the individual nature of the molecules, we can express the structural state of the net corresponding to the nongelified and gelified state in terms of the theory of graphs.

4.3. Nongelified State. We define it as the structural state of a macromolecular system whose corresponding graph is planar.

This definition, with which it is possible to represent a real, finite system in a plane (nonclosed surface or closed surface on a sphere with infinite radius), without intersection of any two cross-links, implies that the components of the real system in a three-dimensional space can be considered completely separately from the point of view of its physical and chemical properties. This holds at a minimal fusion temperature, at a relatively low viscosity and maximum solubility, or even total solubility in an appropriate solvent.

It should be noted that this definition does not prejudice the value of the cyclomatic number of the graph which cannot be zero as certain experimental results show. Thus, cyclical molecules can be soluble, since it is possible to extract them with solvents (see § 3.3.2). On the other hand, the nongelified state is not incompatible with cycles, as the example of dialyl orthophthalate shows [35-42]).

4.4. Gelified State. We define it as the structural state of a macromolecular system whose corresponding graph is nonplanar, i.e., S-topological, provided that the order of S is sufficiently high.

This definition of necessity implies that the cyclomatic number of the graph be nonzero. On the other hand, it makes no hypothesis regarding the connected property of the graph. It results that the ensemble of random graph components can be partitioned into the following subgroups:

— the subgroup of planar components corresponding to the soluble fraction (base fraction);

— the subgroup of nonplanar components corresponding to the insoluble fraction (gel fraction).

For the latter subgroup, the structural state is such that the cyclical chains are no longer separate and that they are more or less branched. In a solvent, for example, their limited separation is translated into a swelling, which itself is progressively limited the more compact the net is i.e., the larger is the cyclomatic number for the same number of corners, either due to a higher rate of evolution, or because there exist a larger number of nodes having a higher functionality in the center of the system.

The concepts of subgroups of planar and nonplanar components is naturally related to linear and cyclomatic complexes defined above. Nevertheless, they do not replace the former because the soluble fraction can contain cyclic molecules (planar).

In general terms, it can be said that the graph corresponding to the gel fraction consists of subgraphs, which are nonplanar and have cyclomatic complexes. Its cyclomatic number v' will, in general, be different from the cyclomatic number v of the graph of the system. The number of its components will depend to the first approximation on the growth mode of the polymer: either in mass or in solution. It can be assumed that with respect to mass, the number of the molecules of the gel fraction will be limited eventually to a single macromolecule (macrogel). In solution, this number can be much larger (microgel [105]). Here, the macromolecules of the gel cannot consist of a single component, but possibly of several components connected to a single molecule by topological and non-planar bonds of the trans-cyclical type (Figure 7 (1) (2) (4) and Figure 8). Even though this type of bond, which was suggested in the study of polysiloxanes [106] and polychlorines of phosphonitrile [107], appear more frequently in the case of linear polymers [108], it is probably much more probable in the case of multifunctional

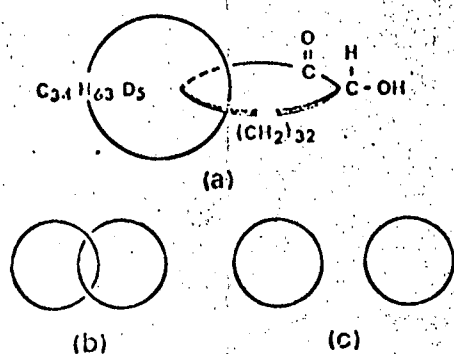


Figure 9. Example of a topological bond.

- (a) 34-34 catenary of Wasserman [109].
- (b) Trans-cyclic isomer (2 components = 1 molecule).
- (c) Exo-cyclic isomer (2 components = 2 molecules).

macromolecules having multiple cycles. This was especially demonstrated in the synthesis of 34-34 catenane [109] (Figure 9). It should not be neglected as one of the possible topological configurations.

The theoretical quantitative evaluation of sol and gel fractions of a random and evolving macromolecular system cannot be done precisely without certain hypotheses which depend on the existence of certain experimental constraints. These hypotheses

will fix the number of molecular components and possibly the cyclomatic number of each of the fractions.

Without any particular constraint and, in the case of a mass change, the most plausible and most suitable hypothesis consists of identifying the gel fraction with the cyclomatic part. This hypothesis amounts to assimilating the soluble fraction in the linear part, i.e., it amounts to excluding the cyclical molecules from the soluble fraction, even the planar ones. This hypothesis is acceptable if it is assumed that the multifunctional cyclical components are very probably not planar because of their random production in space.

5. Structural Condition of Critical Transition.

For a finite, random evolutionary graph, this is the relationship which certain characteristic quantities must satisfy during evolution when passing from the planar graph state to the S-topological graph state.

A S-topological graph is necessarily cyclical, and the problem consists of establishing the necessary condition for the appearance of the first cycle.

Let us consider the most general case of a true, heterogamic graph which is not stoichiometric. If we take into account that the linear chains are not cyclical, the graph can be considered as consisting of an ensemble of nodes with functionality F and an ensemble of branches B_{ij}^k , which belong to the classes B_{ij} , V_k . Let us associate a graph $G = (N, A_p)$ to the graph $G = (M, B_p)$, the corners of which are nodes and the cross-links of which are the branches of G . Each stage of evolution must result in the passage through a certain number of cross-links of class B_{ij} into the class $B_{i-1/j}$, which is of a lower order. The anti-order j is nonevolutive. The sequences of B_{ij} , $i \rightarrow 0$, V_j constitute an ordered partition of the evolutionary connectiveness of the various classes of cross-links towards the total evolutionary connectivity.

According to theorem III, a graph whose corners are nodes of functionality F and the cross-links of which will be produced with equal probability, will of necessity be cyclical if the rate of evolution p satisfies the relationship:

$$p = \frac{2}{F}.$$

For a graph such as \bar{G} and for which the cross-links are not produced with equal probability in time, the cyclization will appear of necessity if the preceding relationship is satisfied for the statistical subgraph. This is true if the pre-cross-links and the anti-cross-links reach the maximum evolutionary connectivity with the greatest probability. Let \bar{p}_Y be the rate of evolution of this subgraph and let b_{ij} be the number of cross-links of class B_{ij} . We have:

$$\bar{p}_Y = \frac{b_{00}}{b_{00} + b_{10} + \sum_{j=1}^{\infty} b_{0j}} = \frac{2}{F}. \quad (22)$$

For the graph G , the second term of this relationship expresses the probability related to the connected branches of the statistical subensemble which is most probable and which is capable of becoming cyclic by evolution.

If P_{ij} are the probabilities associated with the branches of the graph G , and by setting:

$$P_0 = \sum_{j=1}^3 P_{0j}$$

the structural condition for critical transition can be written as:

$$\frac{P_{00}}{P_{00} + P_{10} + P_{01}} = \frac{2}{F}. \quad (23)$$

This relationship immediately defines the statistical cyclical subgraph of \bar{G} which, according to our hypothesis, constitutes the graph for the gelified fraction. It has b_Y cross-links and n_Y nodes such that:

$$\begin{aligned} b_Y &= b(P_{00} + P_{10} + P_{01}) \\ n_Y &= 2b_Y/F. \end{aligned} \quad (24)$$

The cyclomatic number v , which is a topological invariant of G and \bar{G} will be given by the equation for the structural state:

$$\frac{c_Y}{n_Y} - \frac{v}{n_Y} = 1 - \bar{p}_Y \frac{Y}{2}. \quad (25)$$

Its minimum value for $c_Y = 1$ will be the one for the gel fraction which consists of a single component. This possibility exists in the case of a macrogel.

THIRD PART

STOCHASTIC DESCRIPTION

1. Conditions for Random Production.

The conditions for random production of the net of multifunctional macromolecular systems considered here essentially consist of a relationship which is equiprobable in time and space for bonds which can be realized in chemistry between reactive points of monomers.

The corresponding graphs can be described by the evaluation of the proportions of the various categories of branches. They contain all equiprobable realizations of corners and cross-links which make up the branches.

One class of graphs defined by having the same number of consecutive branches can be obtained by a drawing procedure. It consists of drawing the different entities (nodes, anti-nodes, cross-links, pre-cross-links, anti-cross-links) from an urn having a definite composition. The drawing is governed by a law \mathcal{L} which specifies on the one hand, the permitted sequences and, on the other hand, the forbidden sequences which result in returning the drawn entity to the urn. Under these conditions, it can be shown [110] that one obtains an approximation to the probability for the relative proportions of the various categories of possible branches. After each permitted drawing, the initial state of the urn is restored.

These considerations, as well as the resulting calculations, have been described by other authors [111]. We will limit ourselves to describing the main results which makes it possible to establish the equation for critical transition for any system which belongs to

one of these three types considered here using the critical transition structure condition [23]. The study of this equation leads to the calculation of the critical rate of evolution, as well as to the calculation of the possible limits of the existence region for a critical transition as a function of the structural parameters of the particular system under consideration.

2. Homogamic Systems.

Let α be the proportion of points which belong to the multifunctional units. The principal entities can be schematically represented (Figure 10).

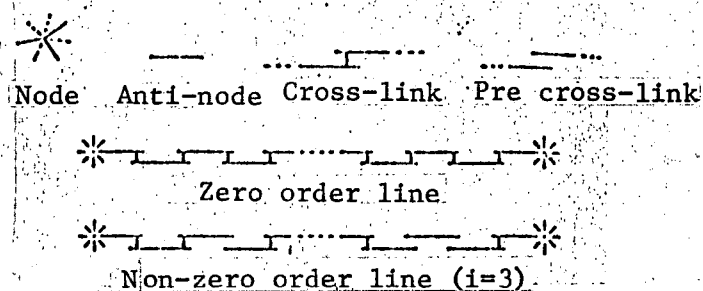


Figure 10. Graph for a homogamic system.
Schematic representation of the principal entities.

2.1. Probabilities Associated With the Various Classes of Branches. Zero order of branches:

$$P_0 = \frac{\alpha p}{1 - p(1 - \alpha)}. \quad (26)$$

First order of branches:

$$P_1 = \frac{\alpha(1 - p)}{[1 - p(1 - \alpha)]^2}. \quad (27)$$

Branches of arbitrary order c :

$$P_c = \alpha \frac{(1 - \alpha)^{c-1} (1 - p)^c}{[1 - p(1 - \alpha)]^{c+1}}. \quad (28)$$

The probabilities associated with the branches B_1^k are shown in Table I.

TABLE I. PROBABILITIES ASSOCIATED WITH THE BRANCHES OF A HOMOGAMIC GRAPH

$i \backslash k$	1	2	3	...	n	...	P_i
0	$\alpha C_1^0 p$	$\alpha(1-\alpha) C_2^0 p^2$	$\alpha(1-\alpha)^2 C_3^0 p^3$...	$\alpha(1-\alpha)^{n-1} C_n^0 p^n$...	$\frac{\alpha p}{1-p(1-\alpha)}$
1	$\alpha C_1^1 (1-p)$	$\alpha(1-\alpha) C_2^1 p(1-p)$	$\alpha(1-\alpha)^2 C_3^1 p^2(1-p)$...	$\alpha(1-\alpha)^{n-1} C_n^1 p^{n-1}(1-p)$...	$\frac{\alpha(1-p)}{[1-p(1-\alpha)]^2}$
2		$\alpha(1-\alpha) C_2^2 (1-p)^2$	$\alpha(1-\alpha)^2 C_3^2 p(2-p)^2$...	$\alpha(1-\alpha)^{n-1} C_n^2 p^{n-2}(1-p)^2$...	$\frac{\alpha(1-\alpha)(1-p)^2}{[1-p(1-\alpha)]^3}$
3			$\alpha(1-\alpha)^2 C_3^3 (2-p)^3$...	$\alpha(1-\alpha)^{n-1} C_n^3 p^{n-3}(1-p)^3$...	$\frac{\alpha(1-\alpha)^2(1-p)^3}{[1-p(1-\alpha)]^4}$
			
c				...	$\alpha(1-\alpha)^{n-1} C_n^c p^{n-c}(1-p)^c$...	$\frac{\alpha(1-\alpha)^{c-1}(1-p)^c}{[1-p(1-\alpha)]^{c+1}}$
			
1^k	$\alpha[p + (1-p)]^{k-1} \alpha$	$\alpha(1-\alpha)[p + (1-p)]^{k-2} \alpha(1-\alpha)$	$\alpha(1-\alpha)^2[p + (1-p)]^{k-3} \alpha(1-\alpha)^2$...	$\alpha(1-\alpha)^{n-1}$...	$\sum_{k=1}^{\infty} \sum_{i=0}^{\infty} P_i^k = 1$

2.2. Critical transition equation. A homogamic system which does not have any branches with an anti-order has the following critical transition structural condition:

$$\frac{P_0}{P_0 + P_{10}} = \frac{2}{F} \quad (29)$$

from which it follows that:

$$\frac{p[1-p(1-\alpha)]}{1-p} = \frac{2}{F-2} \quad (30)$$

For any value of p different from one, we have:

$$p^2(1-\alpha)(F-2) - pF + 2 = 0. \quad (31)$$

2.2.1. Algebraic Solution. This equation always has a root between zero and one. A homogamic system always becomes gelified no matter what its values of the structural parameters are, if the critical rate of evolution is reached:

$$p_c = \frac{F - [\bar{F}^2 - 8(1 - \alpha)(\bar{F} - 2)]^{1/2}}{2(1 - \alpha)(\bar{F} - 2)}. \quad (32)$$

If $\alpha = 1$, the system consists solely of multifunctional units, that is: $p_c = 2/\bar{F}$.

2.2.2. Graphical Solution. The equation can always be put in the form:

$$p^2(1 - \alpha) - p \frac{F}{F - 2} + \frac{2}{F - 2} = 0. \quad (33)$$

It may be advantageous to construct the nomogram (Figure 11) from the two families of curves:

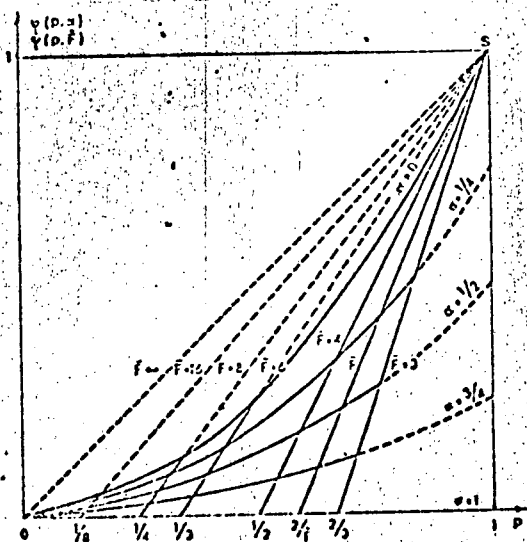


Figure 11. Nomogram for the determination of the critical transition of a homogamic system.

$$\varphi(p, \alpha) = p^2(1 - \alpha) \quad (34)$$

$$\psi(p, F) = p \frac{F}{F - 2} - \frac{2}{F - 2}. \quad (35)$$

This nomogram shows that for a given value of \bar{F} , the value of the critical rate becomes smaller in proportion to the number of multifunctional units. Also, for the same proportion of reactive points, especially for a small proportion, corresponding to multifunctional units, the value of the critical yield decreases very rapidly when the functionality increases. These results justify the fact that gelification appears suddenly in systems which have an average high functionality \bar{f} in a general way. This is true outside of any considerations of chemical kinetics.

3. Pseudoheterogamic Systems.

By α and β , we will designate the proportions of points A and B which belong to multifunctional units. The principal entities can be schematically represented (Figure 12).

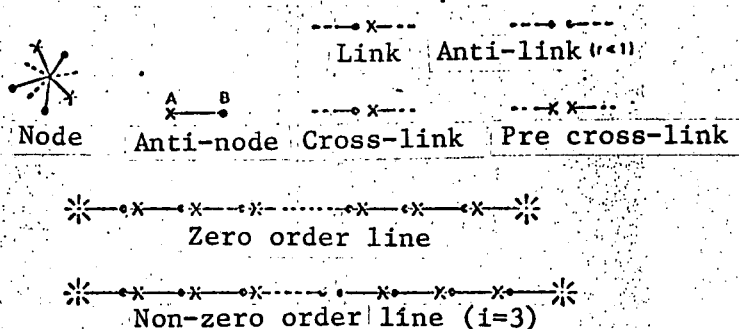


Figure 12. Graph for a pseudo-heterogamic system. Schematic representation of the principal entities.

3.1. Probabilities Associated With the Different Classes of Branches. We assume that $r > 1$ and will express the results as a function of the generalized evolution rate p .

3.1.1. Branches With Anti-Order Zero. Branches of zero order:

$$r_{00} = \frac{\beta p}{1 - p(1 - \beta)} \quad (36)$$

Branches of order one:

$$p_{10} = \frac{\beta \left(\frac{2}{r+1} - p \right)}{[1 - p(1 - \beta)]^2} \quad (37)$$

Branches of arbitrary order c :

$$p_{c0} = \frac{\beta(1 - \beta)^{c-1} \left(\frac{2}{r+1} - p \right)^c}{[1 - p(1 - \beta)]^{c+1}} \quad (38)$$

3.1.2. Branches With Anti-Order One. Branches of order zero:

$$p_{01} = \frac{r-1}{r+1} \frac{1}{1 - p(1 - \beta)} \quad (39)$$

Branches of arbitrary order c :

$$p_{c1} = \frac{r-1}{r+1} \frac{(1 - \beta)^c \left(\frac{2}{r+1} - p \right)^c}{[1 - p(1 - \beta)]^{c+1}} \quad (40)$$

The probabilities associated with the branches B_{ij}^k are collected in Table II. When the value of the stoichiometric ratio is less than one, the probabilities associated with branches B_{ij}^k are obtained from the preceding ones by carrying out the transformations $r \rightarrow 1/r$ and $\beta \rightarrow \alpha$.

3.2. Equations of Critical Transition. The value of the anti-order of branches of a pseudo-heterogamic system cannot be equal to one, and the corresponding structural condition for critical transition is written as:

$$\frac{p_{c0}}{p_{c0} + p_{10} + p_{01}} = \frac{2}{r} \quad (41)$$

from which it follows that:

$$\frac{p[1 - p(1 - \beta)]}{1 - p} = \frac{2}{r-2} \times \frac{r-1 + 2\beta}{\beta(r+1)} \quad (42)$$

or:

$$\frac{p[1 - p(1 - \beta)]}{1 - p} = \frac{2}{r-2} \times R \quad (43)$$

TABLE II. PROBABILITIES ASSOCIATED WITH THE BRANCHES OF A PSEUDO-HETEROGAMIC GRAPH

i	j	k	x	0	1	2	3	...	n	...	P_{ij}
0	0	1	1		$C_1^0 \beta p$	$C_2^0 \beta p \cdot p(1-\beta)$	$C_3^0 \beta p [p(1-\beta)]^2$...	$C_n^0 \beta p [p(1-\beta)]^{n-1}$...	$\beta p / [1-p(1-\beta)]$
0	1	$\frac{r-1}{r+1}$	1		$C_1^0 p(1-\beta)$	$C_2^0 [p(1-\beta)]^2$	$C_3^0 [p(1-\beta)]^3$...	$C_n^0 [p(1-\beta)]^n$...	$1 / [1-p(1-\beta)]$
1	0	1			$C_1^1 \beta \left(\frac{2}{r+1} - p\right)$	$C_2^1 \beta \left(\frac{2}{r+1} - p\right) [p(1-\beta)]$	$C_3^1 \beta \left(\frac{2}{r+1} - p\right) [p(1-\beta)]^2$...	$C_n^1 \beta \left(\frac{2}{r+1} - p\right) [p(1-\beta)]^{n-1}$...	$\beta \left(\frac{2}{r+1} - p\right) / [1-p(1-\beta)]$
1	1	$\frac{r-1}{r+1}$			$C_1^1 (1-\beta) \left(\frac{2}{r+1} - p\right)$	$C_2^1 (1-\beta) \left(\frac{2}{r+1} - p\right) [p(1-\beta)]$	$C_3^1 (1-\beta) \left(\frac{2}{r+1} - p\right) [p(1-\beta)]^2$...	$C_n^1 (1-\beta) \left(\frac{2}{r+1} - p\right) [p(1-\beta)]^{n-1}$...	$(1-\beta) \left(\frac{2}{r+1} - p\right) / [1-p(1-\beta)]$
2	0	1				$C_2^2 \beta (1-\beta) \left(\frac{2}{r+1} - p\right)^2$	$C_3^2 \beta \left(\frac{2}{r+1} - p\right)^2 (1-\beta) [p(1-\beta)]$...	$C_n^2 (1-\beta) \beta \left(\frac{2}{r+1} - p\right)^2 [p(1-\beta)]^{n-2}$...	$\beta (1-\beta) \left(\frac{2}{r+1} - p\right)^2 / [1-p(1-\beta)]$
2	1	$\frac{r-1}{r+1}$				$C_2^2 (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^2$	$C_3^2 (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^2 [p(1-\beta)]$...	$C_n^2 (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^2 [p(1-\beta)]^{n-2}$...	$(1-\beta)^2 \left(\frac{2}{r+1} - p\right)^2 / [1-p(1-\beta)]$
3	0	1					$C_3^3 \beta (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^3$...	$C_n^3 \beta (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^3 [p(1-\beta)]^{n-3}$...	$\beta (1-\beta)^2 \left(\frac{2}{r+1} - p\right)^3 / [1-p(1-\beta)]$
3	1	$\frac{r-1}{r+1}$					$C_3^3 (1-\beta)^3 \left(\frac{2}{r+1} - p\right)^3$...	$C_n^3 (1-\beta)^3 \left(\frac{2}{r+1} - p\right)^3 [p(1-\beta)]^{n-3}$...	$(1-\beta)^3 \left(\frac{2}{r+1} - p\right)^3 / [1-p(1-\beta)]$
						
c	0	1						...	$C_n^c \beta (1-\beta)^{c-1} \left(\frac{2}{r+1} - p\right)^c [p(1-\beta)]^{n-c}$...	$\beta (1-\beta)^{c-1} \left(\frac{2}{r+1} - p\right)^c / [1-p(1-\beta)]^{c+1}$
c	1	$\frac{r-1}{r+1}$...	$C_n^c (1-\beta)^c \left(\frac{2}{r+1} - p\right)^c [p(1-\beta)]^{n-c}$...	$(1-\beta)^c \left(\frac{2}{r+1} - p\right)^c / [1-p(1-\beta)]^{c+1}$
							
1_{00}^k		1			$\beta \frac{2}{r+1}$	$\beta (1-\beta) \left(\frac{2}{r+1}\right)^2$	$\beta (1-\beta)^2 \left(\frac{2}{r+1}\right)^3$...	$\beta (1-\beta)^{n-1} \left(\frac{2}{r+1}\right)^n$...	$\sum_{k=1}^{\infty} \sum_{i=0}^{\infty} P_{00}^k = \frac{2\beta}{r-1+2\beta}$
1_{01}^k		$\frac{r-1}{r+1}$	1		$(1-\beta) \frac{2}{r+1}$	$(1-\beta)^2 \left(\frac{2}{r+1}\right)^2$	$(1-\beta)^3 \left(\frac{2}{r+1}\right)^3$...	$(1-\beta)^n \left(\frac{2}{r+1}\right)^n$...	$\sum_{k=0}^{\infty} \sum_{i=0}^{\infty} P_{01}^k = \frac{r-1}{r-1+2\beta}$

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by setting:

$$R = \frac{r-1+2\beta}{\beta(r+1)} \quad (44)$$

This Equation (43) is, therefore, in the form of Equation (30) for the homogamic system (30) up to a factor of R. This correcting factor takes into account the stoichiometry which stands in a direct relationship with the structural parameters for a pseudo-heterogamic system. In particular, if the system is stoichiometric, the critical transition equation is identical with the one for a homogamic system.

For any value of p different from one, it can be written in the following form:

$$p^2(1-\beta)(\bar{V}-2) - p(\bar{V}-2+2R) + 2R = 0. \quad (45)$$

3.2.1. Algebraic Solution. The critical value of the evolution rate will be given by the root of this equation which corresponds to the possible values of the evolution rate between zero and one, i.e., for values of p such that:

$$0 \leq p \leq \frac{2}{r+1}. \quad (46)$$

This condition is satisfied if:

$$1 \leq r \leq 1 + \beta(\bar{V}-2). \quad (47)$$

In the case where the stoichiometric ratio r is less than one, we would also have:

$$\frac{1}{1 + \alpha(\bar{V}-2)} \leq r \leq 1. \quad (48)$$

In a general way, the critical transition will be possible if the parametric condition for critical transition is satisfied, i.e., if:

$$\frac{1}{1 + \beta(\bar{V}-2)} \leq r \leq 1 + \beta(\bar{V}-2) \quad (49)$$

where ρ is the proportion of minority points which belong to multifunctional units.

The critical transition of necessity is obtained if the critical value of the evolution rate is reached, i.e., for:

$$p_c = \frac{(\bar{F}-2+2R) - [(\bar{F}-2+2R) - 8R(1-\beta)(\bar{F}-2)]^{1/2}}{2(1-\beta)(\bar{F}-2)} \quad (50)$$

If $\beta = 1$, it follows that $\alpha = 1$, and, therefore, $p_c = 2/\bar{F}$.

3.2.2. Graphical Solution. The equation can always be written in the form:

$$p^2(1-\beta) - p \frac{\bar{F}-2+2R}{\bar{F}-2} + \frac{2R}{\bar{F}-2} = 0. \quad (51)$$

As in the preceding case, we can construct the nomogram (Figure 13) from the two families of curves:

$$\phi(p, \beta) = p^2(1-\beta). \quad (52)$$

$$\psi(p, \beta, r, \bar{F}) = p \frac{\bar{F}-2+2R}{\bar{F}-2} - \frac{2R}{\bar{F}-2}. \quad (53)$$

The family of straight lines $\psi(p, \beta, r, \bar{F})$ itself consists of two subfamilies which correspond to the region of permissible values of r for a determined value of \bar{F} . Therefore, on each of the curves of the family $\phi(p, \beta)$, there is a region GL such that the point G is the intersection with $\psi(p, \beta, r, \bar{F})$ for $r = 1$. The point L has the abscissa which corresponds to the intersection of the line $\psi(p, \beta, r, \bar{F})$ for $r = \infty$ with the axis \vec{Op} , that is: $2/[2 + \beta(\bar{F} - 2)]$. The nomogram consists of the trace of the double family of lines [20]:

$$p = \frac{2rp_A}{r+1} = \frac{2p_B}{r+1}$$

which makes it possible to calculate, p_A and p_B .

4. True Heterogamic Systems.

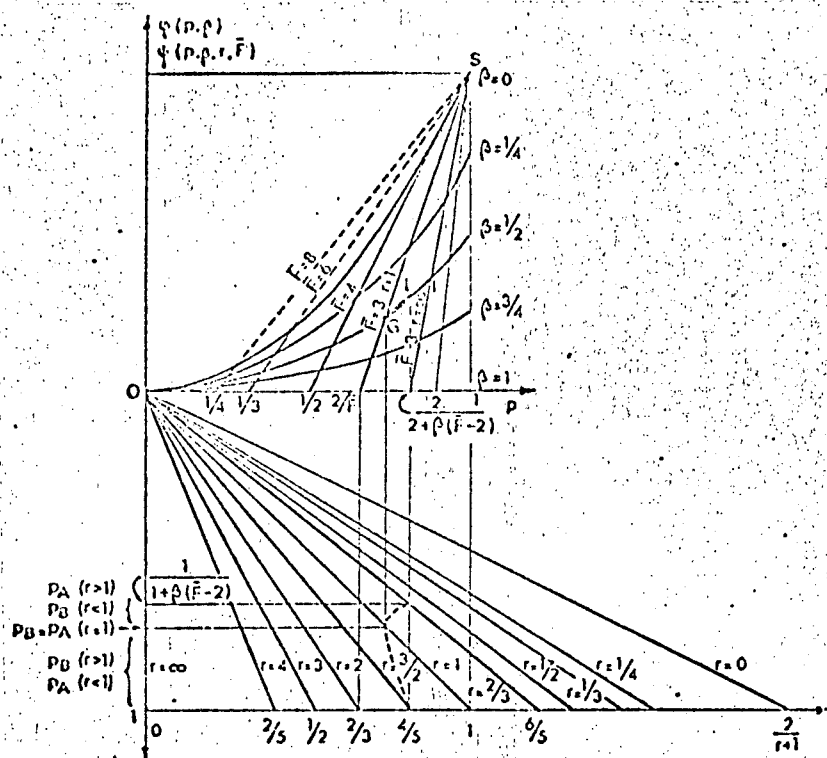


Figure 13. Nomogram for determining the critical transition of a pseudo-heterogrmic system

We will first examine the simple case of stoichiometric systems whose branches do not have an anti-order. The description of non-stoichiometric systems will be obtained from the preceding one by suppressing the elements which were called fictitious. The number of these suppressed elements correspond to the value of the stoichiometric ratio of the system under consideration.

In a general way, because of the particular nature of the repetition mode AA-BB which a median pre-cross-link can have, the various possible branches have two different maximum orders of magnitude, depending on the parity of their minimal ligamic number k , which is connected with the branch type. The principal entities can be schematically represented (Figure 14).

4.1. Stoichiometric Systems

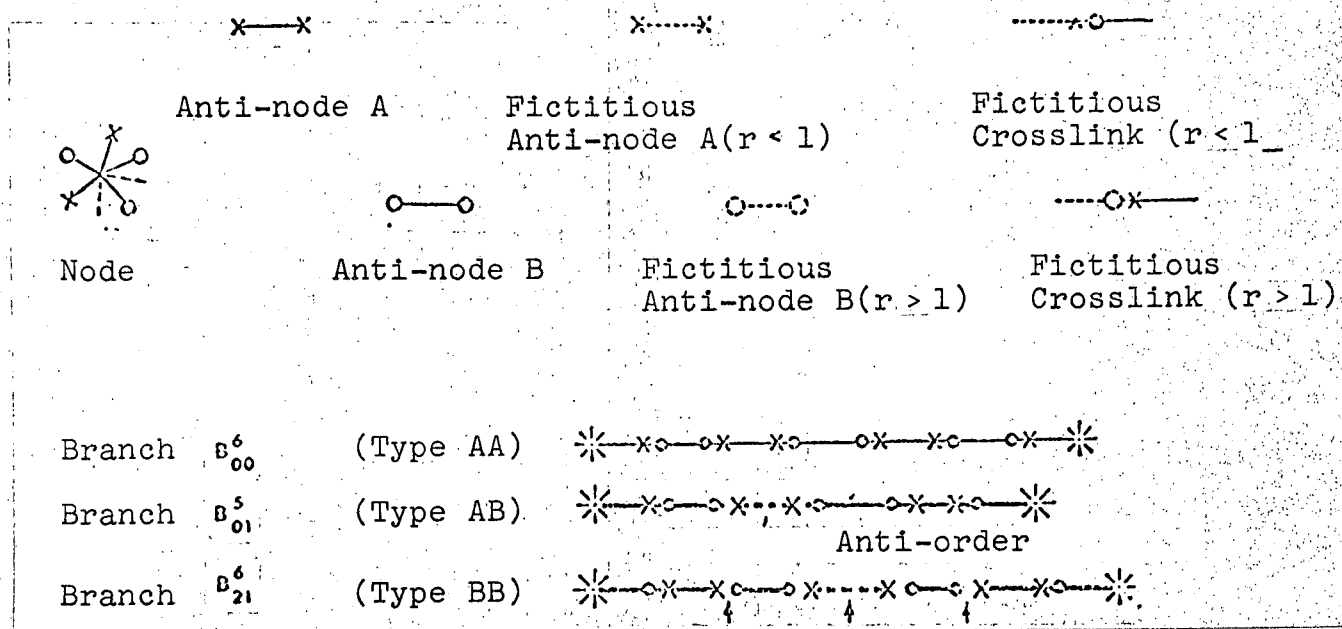


Figure 14. Graph of a true heterogamic system. Schematic representation of the principle entities (example of branches B_{ij}^k).

4.1.1. Probabilities Associated With The Various Classes of Branches. We will now give the general expressions which make it possible to find the probability associated with a class of branches of order given in advance (where zero is considered even).

The expressions for the BB type branches are derived from those of type AA by the transformation $\alpha \leftrightarrow \beta$ in the present case ($r = 1$). We will have, by setting $\beta = (1 - \alpha)$, $(1 - \beta) = \alpha$:

Odd order:

$$P_c^{AA} = \frac{\alpha^2}{\alpha + \beta} p(1-p)^c(1-\alpha)^{\frac{c-1}{2}}(1-\beta)^{\frac{c+1}{2}} \times \frac{(1+x)^{c+1} - (1-x)^{c+1}}{2x(1-x^2)^{c+1}} \quad (54)$$

$$P_c^{AB} = \frac{2\alpha\beta}{\alpha + \beta} (1-p)^c[(1-\alpha)(1-\beta)]^{\frac{c-1}{2}} \times \frac{(1+x)^{c+1} + (1-x)^{c+1}}{2(1-x^2)^{c+1}} \quad (55)$$

Even order:

$$P_0^{AA} = \frac{\alpha^2}{\alpha + \beta} p^2(1-\beta) \times \frac{1}{1-x^2}$$

$$P_{c>0}^{AA} = \frac{\alpha^2}{\alpha + \beta} (1-p)^c(1-\alpha)^{\frac{c-2}{2}}(1-\beta)^{\frac{c}{2}} \times \frac{(1+x)^{c+1} + (1-x)^{c+1}}{2(1-x^2)^{c+1}} \quad (56)$$

$$P_{c>0}^{AB} = \frac{2\alpha\beta}{\alpha + \beta} p(1-p)^c[(1-\alpha)(1-\beta)]^{\frac{c}{2}} \times \frac{(1+x)^{c+1} - (1-x)^{c+1}}{2x(1-x^2)^{c+1}} \quad (57)$$

These results are schematically represented in Table III in which m is such that the number of repetition modes of a branch is equal to $m - 1$.

4.1.2. Equation for Critical Transition. It is immediately derived from the equation for nonstoichiometric systems by setting $r = 1$.

4.2. Nonstoichiometric Systems. We will first assume that the value of the stoichiometric ratio is less than one for convenience of notation. It follows that the proportions of points A belonging to the various monomer units are given by the following:

real nodal points: $r\alpha$.

real anti-nodal points: $r(1 - \alpha)$.

fictitious anti-nodal points: $1 - r$.

TABLE III. PROBABILITIES ASSOCIATED TO THE BRANCHES OF A
TRUE STOICHIOMETRIC HETEROGAMIC GRAPH

m		1		2		3		4		m		$m+1$		P_i
i	Type k	1	2	3	4	5	6	7	8	$2m-1$	$2m$	$2m+1$	$2m+2$	
0	AA		P_0^2		P_0^4		P_0^6		P_0^8	P_0^{2m-1}	P_0^{2m}	P_0^{2m+1}	P_0^{2m+2}	P_0^{AA} P_0^{AB} P_0^{BB}
	AB	P_0^1		P_0^3		P_0^5		P_0^7						
	BB		P_0^2		P_0^4		P_0^6		P_0^8					
1	AA		P_1^2		P_1^4		P_1^6		P_1^8	P_1^{2m-1}	P_1^{2m}	P_1^{2m+1}	P_1^{2m+2}	P_1^{AA} P_1^{AB} P_1^{BB}
	AB	P_1^1		P_1^3		P_1^5		P_1^7						
	BB		P_1^2		P_1^4		P_1^6		P_1^8					
2	AA		P_2^2		P_2^4		P_2^6		P_2^8	P_2^{2m-1}	P_2^{2m}	P_2^{2m+1}	P_2^{2m+2}	P_2^{AA} P_2^{AB} P_2^{BB}
	AB			P_2^3		P_2^5		P_2^7						
	BB		P_2^2		P_2^4		P_2^6		P_2^8					
3	AA				P_3^4		P_3^6		P_3^8	P_3^{2m-1}	P_3^{2m}	P_3^{2m+1}	P_3^{2m+2}	P_3^{AA} P_3^{AB} P_3^{BB}
	AB			P_3^3		P_3^5		P_3^7						
	BB				P_3^4		P_3^6		P_3^8					
4	AA				P_4^4		P_4^6		P_4^8	P_4^{2m-1}	P_4^{2m}	P_4^{2m+1}	P_4^{2m+2}	P_4^{AA} P_4^{AB} P_4^{BB}
	AB					P_4^5		P_4^7						
	BB				P_4^4		P_4^6		P_4^8					
...
$c = 2m-1$	AA									P_c^{2m-1}	P_c^{2m}	P_c^{2m+1}	P_c^{2m+2}	P_c^{AA} P_c^{AB} P_c^{BB}
	AB													
	BB													
$c = 2m$	AA										P_{c+1}^{2m}	P_{c+1}^{2m+1}	P_{c+1}^{2m+2}	P_{c+1}^{AA} P_{c+1}^{AB} P_{c+1}^{BB}
	AB													
	BB										P_{c+1}^{2m}	P_{c+1}^{2m+1}	P_{c+1}^{2m+2}	
...
P^{AAk} P^{ABk} P^{BBk}		P^1	P^2	P^3	P^4	P^5	P^6	P^7	P^8	P^{2m-1}	P^{2m}	P^{2m+1}	P^{2m+2}	$\sum_{k=1}^{\infty} \sum_{i=0}^{\infty} P_i^k = 1$
		P^1	P^2	P^3	P^4	P^5	P^6	P^7	P^8	P^{2m-1}	P^{2m}	P^{2m+1}	P^{2m+2}	

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4.2.1. Probabilities Associated With The Various Classes of Branches.

4.2.1.1. Probabilities Related to Branches With Anti-Order Zero. They are immediately derived from the probabilities associated with the branches of the stoichiometric system by means of the transformations:

$$\begin{aligned} p &\rightarrow p_A \\ \alpha &\rightarrow r\alpha \\ 1-\alpha &\rightarrow r(1-\alpha). \end{aligned}$$

4.2.1.2. Probabilities Related to Branches With Nonzero Anti-Order. The P_{ij}^k are obtained from the P_{i0}^k corresponding to the stoichiometric system by replacing in the branches the real repetition modes by the fictitious repetition modes which consist of a real anti-node of species B and a fictitious anti-node of species A. This is done in a uniform manner. It follows that, in contrast to the order with which all the cross-links are distributed, the anti-order is distributed over all the cross-links. Under these conditions, we can utilize the calculation procedure used for evaluating the probabilities associated with branches of order 1 of the homogamic system beginning with branches of order one.

4.2.1.3. Probabilities Associated With The Branches of Order Zero and Anti-Order Nonzero. These intervene when the equation for critical transition is established. For each type of branch, we designate them by P_0 :

$$P_0 = \sum_k \sum_{j=1}^{\infty} P_{0j}^k \quad (58)$$

The calculations are carried out according to the above procedure which leads to the following results:

$$P_{00}^{AA} = \frac{r^2 \alpha^2 p_A^2 (1-r)(1-\beta)^2}{(r\alpha + \beta)[1-rp_A^2(1-\alpha)(1-\beta)][1-rp_A^2(1-\alpha)(1-\beta) - (1-r)(1-\beta)]} \quad (59)$$

$$P_{00}^{nn} = \frac{\beta^2(1-r)}{(r\alpha + \beta)[1-rp_A^2(1-\alpha)(1-\beta)][1-rp_A^2(1-\alpha)(1-\beta) - (1-r)(1-\beta)]} \quad (60)$$

$$P_{00}^{An} = \frac{2r\alpha\beta p_A(1-r)(1-\beta)}{(r\alpha + \beta)[1-rp_A^2(1-\alpha)(1-\beta)][1-rp_A^2(1-\alpha)(1-\beta) - (1-r)(1-\beta)]} \quad (61)$$

4.2.1.4. Results for the Ensemble. The probabilities associated with the various branches B_{ij}^k can be collected in a table which can be derived from Table III by an appropriate transformation and by adding to it a third dimension corresponding to the values of the anti-order.

In the case where $r > 1$, the results are derived from the preceding ones by the following transformations:

$$\begin{aligned} p_A &\rightarrow p_n \\ \alpha &\rightleftharpoons \beta \\ r &\rightleftharpoons 1/r. \end{aligned}$$

4.2.2. Equation for Critical Transition. The structural condition for a critical transition is written as:

$$\frac{P_{00}}{P_{00} + P_{10} + P_{01}} = \frac{2}{F} \quad (62)$$

from which it follows that, by replacing various terms by their expressions calculated previously:

— If $r < 1$ and by substituting P_A for p :

$$\begin{aligned} &[r^2\alpha^2p^2(1-\beta) + 2\alpha\beta rp + r\beta^2p^2(1-\alpha)][1-rp^2(1-\alpha)(1-\beta)] \\ &[1-rp^2(1-\alpha)(1-\beta) - (1-r)(1-\beta)] / [(2r^2\alpha^2p(1-p)(1-\beta) \\ &+ 2\alpha\beta r(1-p)(1+pr(1-\alpha)(1-\beta)) + 2r\beta^2p(1-p)(1-\beta)] \\ &[1-rp^2(1-\alpha)(1-\beta) - (1-r)(1-\beta)] + (1-r)[r^2\alpha^2p^2(1-\beta)^2 \\ &+ 2\alpha\beta rp(1-\beta) + \beta^2][1-rp^2(1-\alpha)(1-\beta)] = 2/(F-2). \end{aligned} \quad (63)$$

— If $r > 1$, the corresponding equation in which $p = p_B$, is from the above expression by the transformations:

$$\begin{aligned} \alpha &\rightleftharpoons \beta \\ r &\rightleftharpoons 1/r. \end{aligned} \quad (64)$$

These two equations can be expressed either as a function of p_A , or p_B by means of the transformation:

$$rp_A \rightleftharpoons p_B$$

— If $r = 1$, the two preceding equations lead to the following simple equation:

$$\frac{\{x^2 p^2 (1-\beta) + 2\alpha\beta p + \beta^2 p^2 (1-\alpha)\} [1-p^2 (1-\alpha) (1-\beta)] / \{2\alpha^2 p (1-p) (1-\beta) + 2\alpha\beta (1-p) [1+p^2 (1-\alpha) (1-\beta)] + 2\beta^2 p (1-p) (1-\alpha)\}}{2(\bar{r}-2)} \quad (65)$$

4.2.2.1. Algebraic Solution. The following equation is obtained for (63) by ordering it with respect to decreasing powers of p_A :

$$\begin{aligned} & p_A^4 r^3 (1-\alpha)^2 (1-\beta)^2 [rx^2 (1-\beta) + \beta^2 (1-\alpha)] (\bar{r}-2) \\ & - 4p_A^3 \alpha\beta r^3 (1-\alpha)^2 (1-\beta)^2 (\bar{r}-4) \\ & + p_A^4 r^2 (1-\alpha) (1-\beta) \{ (\bar{r}-2) [rx^2 (1-\beta) + \beta^2 (1-\alpha)] \\ & \quad [(1-r) (1-\beta) - 2] + 4\alpha\beta r (1-\alpha) (1-\beta) - 4[r\alpha^2 (1-\beta) + \beta^2 (1-\alpha)] + 2rx^2 (1-r) (1-\beta)^2 \} \\ & + 2p_A^3 r^2 (1-\alpha) (1-\beta) \{ \alpha\beta (\bar{r}-2) [(1-r) (1-\beta) - 2] \\ & \quad + 2[rx^2 (1-\beta) + \beta^2 (1-\alpha)] \} \\ & + p_A^2 r \{ [rx^2 (1-\beta) + \beta^2 (1-\alpha)] [1 - (1-r) (1-\beta)] \\ & \quad (\bar{r}-1-2) + 2(1-r) (1-\beta) \{ 2\alpha\beta r (1-\alpha) (1-\beta) \\ & \quad - rx^2 (1-\beta) + \beta^2 (1-\alpha) \} \} \\ & - 4p_A r \{ [1 - (1-r) (1-\beta)] [\alpha\beta \bar{r} - 2rx^2 (1-\beta) - 2\beta^2 (1-\alpha)] \\ & \quad - 2\alpha\beta (1-r) (1-\beta) \} \\ & - 4\alpha\beta r [1 - (1-r) (1-\beta)] - 2\beta^2 (1-r) = 0. \end{aligned} \quad (66)$$

The critical value of the evolution rate is given by the root of this equation and lies between zero and one. In order for such a root to exist, the various parameters must satisfy a relationship which constitutes the parametric condition for critical transition. One finds that r must satisfy:

$$r_1 \leq r \leq 1 \quad (67)$$

with:

$$\begin{aligned} r_1 = & [2\alpha(1-\beta) - 2\beta + \beta(\bar{r}-2) [2\alpha + \beta(1-\alpha)] \\ & + \{ [2\alpha(1-\beta) - 2\beta + \beta(\bar{r}-2) [2\alpha + \beta(1-\alpha)]]^2 \\ & + 8\alpha\beta(1-\beta) [\alpha(\bar{r}-2) + 2] \}^{1/2} / \{ 2\alpha(1-\beta) [\alpha(\bar{r}-2) + 2] \} \end{aligned} \quad (68)$$

If $\alpha = 0$:

$$r_1 = \frac{2}{(\bar{F} - 2)\beta + 2} \quad (69)$$

If $\beta = 0$

$$r_1 = \frac{2}{(\bar{F} - 2)(\alpha + 1) + 2} \quad (70)$$

In the case where the stoichiometric ratio is larger than one, one finds that r must satisfy the relationship:

$$1 \leq r \leq r_1 \quad (71)$$

with:

$$r_1 = \frac{[2\alpha - 2\beta(1-\alpha) + \alpha(\bar{F} - 2)[2\beta + \alpha(1-\beta)] + \{ [2\alpha - 2\beta(1-\alpha) + \alpha(\bar{F} - 2)[2\beta + \alpha(1-\beta)]^2 + 8\alpha\beta(1-\alpha)[\beta(\bar{F} - 2) + 2] \}^{1/2}}{4\alpha} \quad (72)$$

If $\alpha = 0$;

$$r_1 = \frac{(\bar{F} - 2)\beta + 2}{2} \quad (73)$$

In general terms, critical transition is possible if the double parametric condition for critical transition is satisfied, that is, if:

$$r_1 \leq r \leq r_2 \quad (74)$$

It is always satisfied for a stoichiometric system.

The critical value of the evolution rate, which in the general case consists of a square root between zero and one of the 6th degree equation can be determined by means of a computer in practice.

4.2.2.2. Graphical Solution. Principal Cases. The construction of a nomogram for the general case of a 6th degree equation which depends on 4 parameters, α , β , \bar{F} and r is illusory. However, except for the case $r = 1$, it can be simplified significantly for the case where α or β have values zero or one. The graphical study

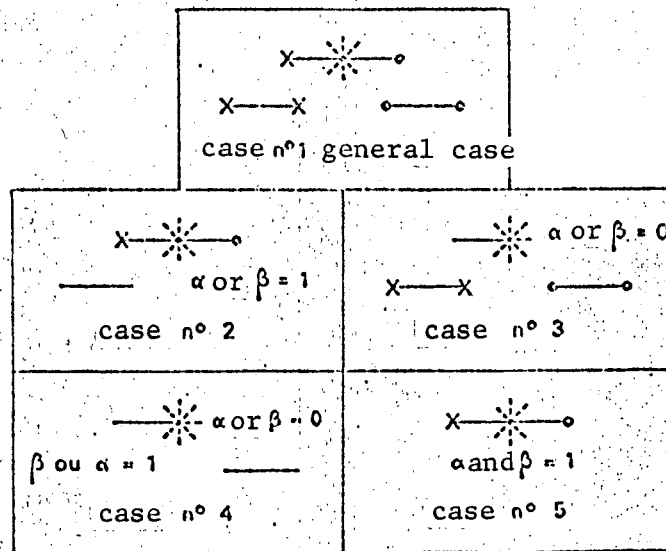


Figure 15. True Heterogramic systems.
Schematic representation of
five principal cases

is then simplified. We can enumerate the following cases:

$$[C_1^2 + C_2^2] = 1 = 8 \text{ principal cases,}$$

where the case ($\alpha = 0, \beta = 0$) has been eliminated, which corresponds to linear systems. For reasons of symmetry $A \rightleftharpoons B$, 4 simple cases can be distinguished, in addition to the general case (Figure 15).

FOURTH PART

EXPERIMENTAL VERIFICATIONS

The experimental values of the gelification points cited in the literature primarily deal with systems which have a simple or relatively simple initial composition with respect to the monomers of the various categories. Also, we have been led to study pseudo-heterogamic base systems, for example, for the undecane hydroxy - 11 system [112] or true heterogamic systems which have many more possible combinations. We will give several results for the latter after reviewing two simple cases.

1. Case No. 4. This corresponds to systems which include multifunctional units A and bifunctional units B. For stoichiometric systems, the critical transition equation is reduced to:

$$p = \frac{2}{F+4} \quad (75)$$

The comparison of theoretical and experimental values of the critical evolution rate is shown in Table IV. Outside of modifications, which are always possible through secondary reactions or by preferential removal of one of the constituents, it seems that the observed deviations from the theoretical model must be attributed to the nonequiprobable spatial behavior. This is due to the primary structure of the reacting agents (flexibility in the spatial structure) and also due to an evolution regime which is more or less removed from the quasi-stationary regime [113].

2. Case No. 3. It corresponds to systems made up of bifunctional units which belong to two species A and B and multifunctional units which belong to a single species, for example, B.

TABLE IV
TRUE HETEROGAMIC SYSTEMS (CASE NUMBER 4)
CRITICAL RATES OF EVOLUTION COMPARED

Stoichiometric systems	p_{th}	p_{ex} (7)
Glycerol ($\bar{F} = 3$) and: phthalic anhydride or acid	0.800	0.786 0.796 (5)
succinic anhydride or acid	0.800	0.760
acidic acid	0.800	0.755
sebacic acid	0.800	0.777
Penta-erythritol ($\bar{F} = 4$) and:		0.606 (8)
adipic acid	0.666	0.63 (19) 0.65 (21)

The equations for critical transition are as follows as a function of the stoichiometric ratio:

$$\frac{p[1 - p^2(1 - \beta)]}{2(1 - p)} = \frac{2}{\bar{F} - 2} \quad (76)$$

$$r < 1 \ (p = p_A):$$

$$\frac{rp[1 - rp^2(1 - \beta)][1 - p^2(1 - \beta)]}{2r(1 - p)[1 - p^2(1 - \beta)] + (1 - r)[1 - rp^2(1 - \beta)]} = \frac{2}{\bar{F} - 2} \quad (77)$$

$$r > 1 \ (p = p_B):$$

$$\frac{p^2[r - p^2(1 - \beta)][1 - p^2(1 - \beta) + \beta(r - 1)]}{2rp(1 - p)[1 - p^2(1 - \beta) + \beta(r - 1)] + r(r - 1)[r - p^2(1 - \beta)]} = \frac{2}{\bar{F} - 2} \quad (78)$$

Critical transition parameter condition:

$$\frac{2}{(\bar{F} - 2)\beta + 2} \leq r \leq \frac{(\bar{F} - 2)\beta + 2}{2} \quad (79)$$

This system was studied especially by Flory [8]. The comparison of theoretical and experimental values is shown in Table V. It is shown that when the value of r is located slightly outside of the theoretical limit, gelification occurs nevertheless. It seems that this is a general phenomenon [114] and leads to nonequiprobable behavior which becomes more sensitive, the farther the system is removed from stoichiometry.

3. Case No. 1 (general case). It corresponds to systems which contain units from species A and from species B in arbitrary proportions and no matter their functionality is. The systems which we have studied consist of points A belonging to adipic and tricarballic acids and points B which belong to diethylene glycol and to pentaerythritol.

The products were purified by several distillations and recrystallizations. Polycondensation was carried out at 154°C (jacket controlled by anisole vapor with boiling) and in a pure nitrogen atmosphere. The nitrogen stream, brought in by a thin tube, extended to the center of reaction. It makes it possible to agitate the medium and decelerate the appearance of gelification by stopping the rising of nitrogen bubbles. The samples taken are dissolved in acetophenone over 2 to 3 hours. The evolution rate of polycondensation is measured by conductimetric dosage of free acid functions using an alcoholic potassium solution.

The values of the evolution rates retained as critical values are limiting values within two limits: a smaller upper limit corresponds to samples which have the smallest insoluble fraction and a larger lower limit, which corresponds to the maximum value of the evolution rate of the samples which are completely soluble. Taking the experimental errors of dosage into account, the values are only given to ± 0.005 .

The composition of the systems is determined by several weighings, which corresponds to the successive introduction of constituents in the polycondensation tube. This makes it possible to calculate the four parameters α , β , r , \bar{F} of the general equation.

TABLE V
TRUE HETEROGAMIC SYSTEMS (CASE NO. 3). CRITICAL
RATES OF EVOLUTION COMPARED

Gelification Points					
	Experimental		Theoretical		
Tricarboic acid ($\bar{F} = 3$)					
Glycol diethylene and:					
adipic acid	1.000	0.293	0.911	0.904	0.007
succinic acid	1.000	0.194	0.939	0.929	0.010
succinic acid	1.002	0.404	0.894	0.883	0.011
adipic acid	0.800	0.375	0.9907	non gel.	0.009
				($r < 0.842$)	
adipic acid	0.800	0.250	non gel	non gel	0.000
				($r < 0.888$)	

TABLE VI
TRUE HETEROGAMIC SYSTEMS (CASE NO. 1 OR GENERAL CASE). CRITICAL
RATES OF EVOLUTION COMPARED

Expt. No.	$r = \frac{ \text{sites} - \text{COOH} }{ \text{sites} - \text{OH} }$	α	β	\bar{F}	P_{ex}	P_{th}	$\delta = P_{ex} - P_{th} $
1	0,974	0,599	0,605	3,000	0,745	0,749	0,004
2	0,935	0,200	0,610	—	0,800	0,805	0,005
3	0,979	0,599	0,210	—	0,815	0,807	0,008
4	0,982	0,403	0,599	—	0,780	0,773	0,007
5	0,956	0,599	0,415	—	0,785	0,780	0,005
6	1,114	0,268	0,204	—	0,810	0,816	0,006
7	0,939	0,393	0,100	—	0,800	0,797	0,003
8	0,981	0,600	0,782	3,359	0,665	0,656	0,009
9	0,969	0,608	0,780	3,223	0,690	0,686	0,004

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The comparison of the experimental values and the theoretical values calculated from Equation (63) and its transformation (64) (*), is given in Table VI rounded to the third decimal.

The agreement of the results is on the order (1 part per 100) or very close (< 2 per 100) of the experimental error which is estimated. For systems close to stoichiometry studied here, it is not possible to detect a noticeable deviation in behavior from the theoretical model.

(*) Calculations carried out on the CAB 500 computer (P.A.F. system).

FIFTH PART

APPLICATIONS OF THE THEORY

In addition to the important concepts of critical transition and the region of existence of this transition which can be determined, the present theory can interpret certain phenomena. Certain techniques can be developed as well. It is also possible to determine certain average values, the knowledge of which may be desirable in measurements and which can be verified experimentally. Above this, it is possible to generalize the theory to the case where the systems comprise monofunctional monomer units or monomers which have points which are not equally reactive. This can be done by starting with the initial scheme.

The complete development of these different questions would be outside of the framework of the report. We shall limit ourselves to certain brief indications.

1. Reticulation, Vulcanization.

Reticulation and vulcanization must be considered less as phenomena than as particular techniques associated with the general phenomenon of gelification. In effect, they consist in an evolution of the structure of a macromolecular multifunctional compound which has a planar graph towards the structure which has a nonplanar graph, beginning with a state which is different from state I of the ensemble of the disjoint monomers.

The description of the reticulation or vulcanization processes thus leads to a description of the type described above. The origin of evolution is taken as the state corresponding to that of the

partial graph $G = (M, R_p)$. This is state I of a graph whose disjoint "apexes" are made up by the ensemble of the components of $G = (M, R_p)$. The functionality of these apexes becomes higher, the larger p becomes. Frequently in practice, the state of the initial system is modified beginning with the origin of the process by the addition of a reticulating agent which, in general, consists of bifunctional monomers. The reactive points of the reticulating agent can belong to any of the species presented in connection with the initial polymer. In particular, it can belong to a species which has remained latent during the development of the polymer and which can react under the physical and chemical conditions imposed. If, for example, in the case of unsaturated polyesters, the different type of bonds are established simultaneously, the complete description of the process results in the superposition of the evolution processes for the two systems (homogamic and heterogamic).

In general, vulcanization must be considered as a reticulation limited to its origin which allows a certain superposition of characteristics, especially mechanical ones, which belong to each of the linear and cyclical structures.

Depending on the type of bonds coming into play, the reticulation and vulcanization can be quantitatively interpreted by using one of the models proposed previously [115].

2. Average Molecular Quantities.

The numerical values of average molecular quantities are obtained directly from reduced state equations. Constraints which are inherent to the real systems under consideration must be taken into account. The evaluation of the sol and gel fractions, as well as the molecular quantities, assume certain theoretical or experimental hypotheses regarding the connectivity of the gel fraction. They may also involve the value of the cyclomatic member of each of these fractions.

On the other hand, the statistical description adapted here makes it possible to obtain one additional piece of information:

this is the distribution of molecules of the soluble fraction into ramified molecules and linear molecules. In effect, a ramified component of G corresponds to a ramified component of \bar{G} (see Second Part, 5). But $(i + j - 1)$ linear floating chains in G correspond to a cross-link of class B_{ij} and \bar{G} .

Finally, if the most likely form of distribution is taken into account, it will be possible to calculate the different average molecular quantities which are used in experiments in general (average with respect to weight, average with respect to z , etc.).

3. Systems Consisting of Monofunctional Units.

The statistical description of such systems immediately results from the description given previously, if it is noted that one can assimilate the collection of monofunctional units from an arbitrary number F' into a fictitious node having functionality F' whose decomposition into its parts leads to as many corners as are definitely pending. The corresponding supporting graph will have two new types of branches in addition to the classical types and independent of their connected nature:

— branches which have two fictitious nodal extremities (floating branches), which will make up linear floating chains with nonreactive extremities of the real graph at saturation;

— branches which have a real nodal extremity and a fictitious nodal extremity (pending branches) which make up pending branches with nonreactive extremities of the real graph at saturation.

The fictitious functionality F' cannot intervene in the estimation of the average nodal functionality \bar{F} of the real graph. On the other hand, a pair of pending branches, for example, of order zero, must be assimilated into a classic branch of order zero and anti-order one. In particular, this occurs because of this new term which will be modified due to the structural condition of critical transition.

4. Systems Which Include Points With Different Reactivity.

If, for certain appropriately chosen chemical systems, it can be assumed that for a sufficient degree of approximation bonds are established in the course of time and in space in an equiprobable manner, then, in general, the bonds will be created under the influence of various factors. This will depend on energy, steric properties, etc. These various constraints make it possible to classify the bonds according to reactivity of the points between which they are established and in relationship to each other. The reactivity, or preferential capability of establishing a class of bonds, could, therefore, be expressed in terms of probabilities.

Let us consider a heterogamic system whose points B correspond, for example, to various species B_i which have different reactivities according to some proportion x_i .

If p_i is the proportion of points of species B_i which have reacted at a given moment, it is possible to define a relative coefficient of reactivity r_i of points from species B_0 which have the smallest reactivity and with respect to points of species B_i such that:

$$p_0 = r_i p_i$$

This coefficient only has a meaning in an evolution region which corresponds to a proportion of points B_i involved in the reaction which is less than one.

The probability that a permissible bond will be established between a point A and a point B_i will be:

$$P_{AB_i} = \sum_i x_i p_i = p_0 \sum_i x_i r_i$$

where the index i depends on the distribution of the various species among the corners. Thus, it is possible to express the various

relationships describing the system as a function of p_0 , the rate of evolution taken with respect to the least reactive species. It is also a function of the known proportions X_1 and the coefficients r_1 which are known or assumed known.

5. Degradation.

As we have already indicated, degradation is the process which is inverse to the process of synthesis. The statistical description of a macromolecular multifunctional system during degradation follows immediately from the preceding considerations by replacing the generalized evolution rate p by its complementary term d , which is the generalized rate of degradation.

In the case where the initial state of the system is such that the corresponding graph is not planar, it is possible to predict a point of degelification.

If the rupture of the bonds does not take place a priori in an equiprobable way, the preceding remarks would have to be taken into account.

It is possible to give a statistical description using the presented theory of the degradation of systems which are not macromolecular systems in the proper sense. Thus, the degrading evolution of a random graph whose linear components have tetrafunctional and monofunctional corners represents a model of thermal cracking, which possibly can be hydrogenating, of "heavy" hydrocarbons for which it is particularly simple to give a statistical description.

CONCLUSION

The experimental data surrounding the phenomenon of gelification lead to research regarding the random evolutive structure of the molecular network which develops in the course of the chemical reaction based on the system of molecules.

We have examined the behavior of macromolecular multifunctional systems from the structural and stochastic point of view. The structural or topological aspect encompasses the totality of possible configurations of structure in the sense of Konig in a straight forward manner. The stochastic aspect describes the chemical reaction at each moment of the evolution in the form of a random distribution of bonds which are chemically possible between reactive functions carried by the molecules. This point of view leads us to distinguish two particular classes of systems which obviously exist: homogamic systems for which the chemical bonds are made between arbitrary pairs of points and heterogamic systems for which, on the other hand, the bonds are formed in a specific manner.

The elementary given data of the theory of graphs make it possible to give an axiomatic definition for the important concepts involving intermolecular and intramolecular bonds. This is also true for the gelified and nongelified state. We were able to establish that the passing from one state to another must necessarily take place during the evolution. Certain characteristic quantities of the system graph, which are functions of its structural parameters and its evolution rate, satisfy a particular relationship which is called the structural condition for critical transition. The study of this relationship shows that it cannot always be satisfied, particularly for heterogamic systems. Consequently, when bonds are formed in a specific manner, gelification cannot be produced when the ratio of the number of complementary points present satisfies two inequalities, which are called parametric condition of critical

transition. The latter takes into account the average functionality and the proportion of each species of points which belong to the nodes of the net.

When this condition is satisfied in the case of heterogamic systems which are quasi-stoichiometric, we were able to experimentally verify the fact that the gelification points can be theoretically predicted with an accuracy of the order 1 part per 100 for various values of the structural parameters.

Among the various application possibilities and generalizations of the theory, we should note the following two immediately: the inclusion of reticulation and vulcanization in a special case of the gelification phenomenon and the calculation of various average molecular quantities (in number, in weight, in z , etc.) should be mentioned. This is true, not only for the insoluble fraction when it exists, but also true for the linear part and for the ramified part of the soluble fraction.

The generalization of the theory to systems which comprise monofunctional units is possible due to simple assimilation. It is implicitly contained in the statistical method of description of the net and consists of identifying the monofunctional entities with fictitious nodal extremities.

Elsewhere, we were able to show that the possible nonequilibrium reactivity of chemical functions can be expressed in terms of probability.

Finally, since it was independent of the direction of evolution selected, the present stochastic description also constitutes a theory of degradation of macromolecular multifunctional compounds.

The present theory, as well as previous ones, could be generalized to chemical compounds having various origins. It was established for the study of macromolecular organic compounds. It is sufficient to consider the fact that the nature of the bond is, for example, electrovalent, or of the secondary type such as a hydrogen bond, or

of the Van der Waals interaction type. It would also be possible to consider evolutionary systems from the same theoretical point of view which would lead to synthetic or natural inorganic gels, organic gels having an animal or vegetable origin or, finally, certain transitory relationships with living matter such as the antigen-antibody system.

It may be seen paradoxical that the systematic study of the gelification region does not seem to have been the object of a large number of papers in macromolecular chemistry [113] [114]. It is a discipline in which the gelification region (precipitation) is constantly being studied. This is also due to the method of experimentation. This is the case in immunology where one of the major problems is the study of the precipitation region of the antigen-antibody complex. This region is located between a zone of excess antigens and a zone of excess antibodies or inhibition zones. Even though the problem is not simple, the important results obtained by the Pasteur School regarding the multispecific nature of multifunctional antigens and the monospecificity of various types of bifunctional antibodies [116] will lead to an interpretation of the behavior of the antigen-antibody system according to a true heterogamic system comprising several types of bonds (specificity). Consideration of cyclic structures will make it possible to place it within the framework of the net theory of Pauling [117].

As can be seen, the theory and its application possibilities shown here is located halfway between the activities of chemists, physical chemists, biologists and mathematicians. In order to develop and describe it, an involved terminology had to be used which can satisfy no one. We do not mean to say that it is a definite theory, just like any other theory. Primarily, we wanted to show that the theory of graphs could contribute to the knowledge of the random structure of macromolecular compounds. We wish to suggest to others a particularly important application of combinatory topology. We wanted to expose in a general way the theory of graphs in its topological relationship with three-dimensional space (theory of nodes). Unfortunately, it is not well known by nonspecialists.

of nodes). Unfortunately, it is not well known by nonspecialists. We hope we have reached our goal.

"In our efforts to understand reality, we are similar to a person trying to understand the mechanism of a closed watch. He sees the dial and the moving hands. He hears the tick-tock, but he has no way to open the case. If he is ingenious, he can think of a mechanism which can explain all of the observed facts. However, it is possible for him to ever be certain that the idea he has is the only one which can explain the facts he has observed".

A. Einstein and L. Infeld
(The Evolution of Ideas in Physics)

REFERENCE

1. G. Champetier. — *Macromolecular Chemistry*. Armand Colin, Edit., Paris, 1957.
2. W. H. CAROTHERS. — *Trans. Faraday Soc.*, 1936, 32, 44.
3. R. H. KIENLE et A. G. HOVEY. — *J. Am. Chem. Soc.*, 1929, 51, 509.
4. R. H. KIENLE, P. A. VAN DER MEULEN et F. E. PETKE. — *J. Am. Chem. Soc.*, 1931, 61, 2258.
5. R. H. KIENLE, P. A. VAN DER MEULEN et F. E. PETKE. — *J. Am. Chem. Soc.*, 1931, 61, 2268.
6. R. H. KIENLE et F. E. PETKE. — *J. Am. Chem. Soc.*, 1940, 62, 1653.
7. R. H. KIENLE et F. E. PETKE. — *J. Am. Chem. Soc.*, 1941, 63, 481.
8. P. J. FLORY. — *J. Am. Chem. Soc.*, 1941, 63, 3083.
9. P. J. FLORY. — *J. Am. Chem. Soc.*, 1941, 63, 3091.
10. P. J. FLORY. — *J. Am. Chem. Soc.*, 1941, 63, 3096.
11. P. J. FLORY. — *J. Phys. Chem.*, 1942, 46, 132.
12. P. J. FLORY. — *J. Chem. Phys.*, 1944, 12, 125.
13. P. J. FLORY. — *J. Am. Chem. Soc.*, 1939, 61, 3334.
14. P. J. FLORY. — *J. Am. Chem. Soc.*, 1940, 62, 1057.
15. P. J. FLORY. — *J. Am. Chem. Soc.*, 1940, 62, 2255.
16. G. CHAMPETIER et R. VERGOZ. — *Rec. Trav. Chim. Pays-Bas*, 1950, 69, 85.
17. T. F. BRADLEY. — *Ind. Eng. Chem.*, 1938, 30, 689.
18. T. F. BRADLEY et H. F. PFANN. — *Ind. Eng. Chem.*, 1940, 32, 694.
19. L. L. WEIL et H. JACOBSON. — Résultats cités dans *Advancing Fronts in chemistry*. S. B. Twiss, Edit., Reinhold Publishing Corp. New York, 1943, chap. 6, par W. H. STOCKMAYER.
20. W. H. STOCKMAYER et L. L. WEIL. — *Id.*
21. F. T. WALKER et T. MACKAY. — *J. Oil and Colour Chem. Ass.*, 1951, 34, 311.
22. I. WALTHER et I. MILLER. — *J. Am. Chem. Soc.*, 1955, 77, 3006.
23. W. H. STOCKMAYER. — *J. Chem. Phys.*, 1943, 11, 45.
24. W. H. STOCKMAYER. — *J. Chem. Phys.*, 1944, 12, 125.
25. H. JACOBSON et W. H. STOCKMAYER. — *J. Chem. Phys.*, 1950, 18, 1600.
26. F. E. HARRIS. — *J. Chem. Phys.*, 1955, 23, 1518.
27. R. W. KILB. — *J. Chem. Phys.*, 1958, 62, 969.
28. F. P. PRICE, J. H. GIBBS et B. H. ZIMM. — *J. Chem. Phys.*, 1958, 62, 972.
29. F. P. PRICE. — *J. Chem. Phys.*, 1958, 62, 977.
30. B. H. ZIMM, F. P. PRICE et J. P. BIANCHI. — *J. Chem. Phys.*, 1958, 62, 979.
31. H. STAUDINGER et W. HEUER. — *Ber.*, 1935, 68, 1618.
32. R. G. W. NORRISH et E. F. BROOKMAN. — *Proc. Roy. Soc.*, 1937, A 163, 205.
33. W. H. STOCKMAYER et H. JACOBSON. — *J. Chem. Phys.*, 1943, 11, 393.
34. C. WALLING. — *J. Am. Chem. Soc.*, 1945, 67, 441.
35. W. SIMPSON. — *J. Soc. Chem. Ind.*, 1946, 65, 107.
36. W. SIMPSON, T. HOLT et R. ZETIE. — *J. Polym. Sci.*, 1953, 10, 489.
37. W. SIMPSON et T. HOLT. — *J. Polym. Sci.*, 1955, 18, 335.
38. T. HOLT et W. SIMPSON. — *Proc. Roy. Soc.*, 1953, A 6 B, n° 238, 356.

39. R. N. HAWARD. --- *J. Polym. Sci.*, 1954, 14, 535.
40. M. GORDON. --- *J. Chem. Phys.*, 1954, 22, 610.
41. M. GORDON, B. M. GRIEVESON et I. D. McMILLAN. --- *Trans. Faraday Soc.*, 1956, 52, 1012.
42. M. GORDON et R. J. ROE. --- *J. Polym. Sci.*, 1956, 21, 27.
43. M. GORDON et I. D. McMILLAN. --- *Die Makromol. Chem.*, 1958, 23, 188.
44. L. MINNEMA et A. J. STAVERMAN. --- *J. Polym. Sci.*, 1958, 29, 281.
45. H. S. LILLEY. --- *Paint Technol.*, 1958, 441.
46. L. C. CASE. --- *J. Polym. Sci.*, 1957, 26, 383.
47. L. C. CASE. --- *J. Polym. Sci.*, 1958, 29, 443.
48. L. C. CASE. --- *J. Polym. Sci.*, 1959, 37, 155.
49. L. C. CASE. --- *J. Polym. Sci.*, 1960, 43, 27.
50. A. DI GIACOMO. --- *J. Polym. Sci.*, 1960, 47, 435.
51. S. ERLANDER et D. FRENCH. --- *J. Polym. Sci.*, 1956, 20, 7.
52. E. S. ALLEN. --- *J. Polym. Sci.*, 1956, 21, 349.
53. M. JONASON. --- *J. Appl. Polym. Sci.*, 1960, 4, 129.
54. P. J. FLORY et J. REHNER, Jr. --- *J. Chem. Phys.*, 1943, 11, 512.
55. P. J. FLORY et J. REHNER JR. --- *J. Chem. Phys.*, 1943, 11, 521.
56. J. R. SCHAEFFGEN et P. J. FLORY. --- *J. Am. Chem. Soc.*, 1948, 70, 2709.
57. J. R. SCHAEFFGEN et P. J. FLORY. --- *J. Am. Chem. Soc.*, 1950, 72, 689.
58. H. S. LILLEY et D. W. J. OSMOND. --- *Paint. Technol.*, 1948, 13, 217.
59. C. A. J. HOEVE. --- *J. Polym. Sci.*, 1956, 21, 1.
60. C. A. J. HOEVE. --- *J. Polym. Sci.*, 1956, 21, 11.
61. C. A. J. HOEVE et D. A. SUTTON. --- *J. Am. Oil Chem. Soc.*, 1956, 33, 312.
62. T. KAKIHAI et T. NOGUCHI. --- *Kogyo, Kagaku Zasshi*, 1961, 64, 398.
63. Y. TANAKA et H. KAKIUCHI. --- *J. Appl. polym. Sci.*, 1963, 7, 1851.
64. E. INOTO. --- *Kobunshi Tenbo*, 1950, 2, 226.
65. F. G. A. STONE et W. A. G. GRAHAM. --- *Inorganic Polymers*. Acad. Press, 1962.
66. F. G. R. GIMBLETT. --- *Inorganic Polymer Chemistry*. Butterworth and Co. Publishers, 1963.
67. J. E. ELDRIDGE et J. D. FERRY. --- *J. Phys. Chem.*, 1954, 58, 992.
68. R. J. GOLDBERG et J. W. WILLIAM. --- *Disc. Faraday Soc.*, 1952, 13, 224.
69. R. J. GOLDBERG. --- *J. Am. Chem. Soc.*, 1952, 74, 5715.
70. R. J. GOLDBERG. --- *J. Am. Chem. Soc.*, 1953, 75, 3127.
71. T. AMANO, I. SYOZI, T. TOKUNAGA et S. SATO. --- *Biken Journal*, 1962, 5, 259.
72. M. T. PALMITER et F. ALADJEM. --- *J. Theoret. Biol.*, 1963, 5, 211.
73. M. GORDON. --- *Proc. Roy. Soc. (London)*, 1962, A 268, 240.
74. I. J. GOOD. --- *Proc. Cam. Phil. Soc.*, 1948, 45, 360.
75. I. J. GOOD. --- *Proc. Roy. Soc. (London)*, 1963, A 272, 54.
76. T. E. HARRIS. --- *The theory of Branching Processes*. Springer-Verlag, Berlin, 1963.
77. M. GORDON et G. R. SCANTLEBURY. --- *Trans. Faraday Soc.*, 1964, 60, 604.
78. G. R. DONSON et M. GORDON. --- *J. Chem. Phys.*, 1964, 41, 2389.
79. G. R. DONSON et M. GORDON. --- *J. Chem. Phys.*, 1965, 43, 705.

80. M. Gordon and G. R. Scantlebury. — Pre-tirage No. 513. International Symposium on Macromolecular Chemistry, Prague, 1965 J. Polym, Sci. (to be published).
81. P. WHITTLE. — *Proc. Camb. Phil. Soc.*, 1965, 61, 475.
82. P. WHITTLE. — *Proc. Roy. Soc. (London)*, 1965, A 285, 501.
83. P. ERDOS et A. RENYI. — *Publ. Math. Inst. Hungar. Acad. Sci.*, 1960, 5, 17-61.
84. H. L. FRISCH, J. M. HAMMERSLEY. — *J. Soc. Indust. Appl. Math.*, 1963, vol. 11, n° 4, 894-918.
85. T. Vogel. — *Theory of Evolutionary Systems*. Gauthier-Villars, Edit., Paris, 1965.
86. D. König. — *Theory of Finite and Infinite Graphs*. Akad. Verl. M. B. H., Leipzig, 1936 and Chelsea, New York, 1950.
87. G. POLYA. — *C. R. Acad. Sci.*, 1935, 201, 1167.
 — — *C. R. Acad. Sci.*, 1936, 202, 1554.
 — — *Helv. Chim. Acta*, 1936, 19, 22.
 — — *Z. Krist.*, 1936, 93, 415.
 — — *Acta Math.*, 1937, 63, 145.
88. T. L. HILL. — *J. Phys. Chem.*, (1943), 47, 253.
 — — *J. Chem. Phys.*, (1943), 11, 294.
89. E. N. Albino of Chossione. — *Fundamental Numbers of Graphs and Incident Matrices in Organic Chemical Compounds*. These Université de Buenos Aires, Argentina, 1962.
90. D. W. MATULA, L. C. D. GROENWEGHE et J. R. VAN WAZER. — *J. Chem. Phys.*, 1964, 41, 3105.
91. C. Berge. — *Theory of Graphs and Applications*. Dunod, Paris, 1963.
92. G. A. DIRAC. — *J. London Math. Soc.*, 1956, 31, 460, cité en (91).
93. S. LERSCHERZ. — *Introduction to topology*. Princeton University Press, Princeton, 1949.
94. C. Berge and A. Ghoulia-Houri. — *Programs, Games and Transport Networks*. Dunod, Paris, 1962.
95. C. K. INGOLD. — *Structure and Mechanism in Organic Chemistry*. Cornell University Press Ithaca, New York, 1953.
96. L. PAULING. — *The nature of the Chemical bond*. Third Edition. Cornell University Press, Ithaca, New York, 1960.
97. H. ZAHN et H. SPÖR. — *Chem. Ber.*, 1959, 92, 1375.
98. H. ZAHN et F. SCHMIDT. — *Chem. Ber.*, 1959, 92, 1381.
99. P. H. HERMANS. — *Nature*, 1956, 177, 127.
100. P. H. HERMANS. — *Nature*, 1956, 177, 126.
101. H. JACOBSON, C. O. BECKMANN et W. H. STOCKMAYER. — *J. Chem. Phys.*, 1950, 18, 1607.
102. S. D. ROSS, E. R. CORBURN, W. A. LEACH et W. E. ROBINSON. — *J. Polym. Sci.*, 1954, 13, 406.
103. W. PATNODE et D. F. WILCOCK. — *J. Am. Chem. Soc.*, 1946, 68, 358.
104. C. J. BROWN, A. HILL et P. V. YOGLE. — *Nature*, 1956, 177, 128.
105. W. O. BAKER. — *Ind. Eng. Chem.*, 1949, 41, 511.
106. H. FRISCH, I. MARTIN et H. MARK. — *Monatsh.*, 1953, 84, 250.
107. F. PATAY et P. DERST. — *Angew. Chem.*, 1959, 71, 105.
108. H. L. FRISCH et E. WASSERMAN. — *J. Am. Chem. Soc.*, 1961, 83, 3789.
109. E. WASSERMAN. — *J. Am. Chem. Soc.*, 1960, 82, 4433.

110. H. Raynaud. — Thesis for the Doctor of Sciences in Mathematics, Paris, 1966 (to be published).
 111. C. M. Bruneau. — French Review of Information Processing (R. F. T. I.). Chiffres. 1966, Vol. 9, No. 3, p. 201-233.
 112. C. M. Bruneau. — Nonpublished Results (to be published).
 113. G. R. Scantlebury. — Thesis at the University of London, 1965.
M. Gordon and G. R. Scantlebury. — J. Chem. Soc. London, 1966 (to be published).
 114. C. M. Bruneau and P. Burgaud. — Nonpublished Results (to be published).
 115. C. M. Bruneau. — International Symposium of Macromolecular Chemistry. Prague, 1965. J. Polym. Sci. (to be published).
-
116. C. LAPRESLE. — *Ann. Inst. Pasteur*, 1955, 89, 654.
 117. L. PAULING. — *J. Am. Chem. Soc.*, 1940, 62, 2643.
 118. M. L. HIGGINS. — *Sheet Polymers and Network Polymers*. Conférence principale: *Symposium international de Chimie macromoléculaire*. Prague (1965). *J. Polym. Sci.* (à paraître).